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# POLYMER ALLOYS AND BLENDS

by

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CONTENTS


**1. Introduction** (definition of basic terms, historical developments and scope).

**2. Thermodynamics of Polymer Blends**

2.1 Basic relations

2.2 Polymer/polymer miscibility

2.3 Dynamics of phase separation

2.4 Methods for determination of solubility

2.5 Compatibilization

2.6 Thermodynamically imposed structures

**3. Melt Flow of Polymer Blends**

3.1 Basic relations

3.2 Influence of miscibility on low-deformation rate flow behavior (composition dependence)

3.2.1 Miscible blends

3.2.2 Immiscible blends

3.2.2.1 Model systems
3.2.2.2 Newtonian behavior of immiscible blends and alloys

3.3 Small strain flow behavior

3.3.1 Yield stress

3.3.2 Structural and time effects

3.4 Large strain flows

3.4.1 Steady state shear flow

3.4.2 Uniaxial extensional flow behavior of PAB

3.5 Flow-imposed morphology

**4. The Morphology of Immiscible Polymer Blends During Processing**

4.1 Introduction

4.2 Determination of PAB Morphology by Microscopic Techniques (LM and EM)

4.3 Droplet breakup in well-defined flow fields

4.4 The influence of material properties on particle breakup during processing

4.5 The effect of processing parameters in compounding and shaping operations on PAB morphology

**5. References**

## 1. INTRODUCTION

The terms: blend and alloy describe intimate mixtures of ingredients. However, while "blend" may indicate a true molecular solution, (viz. blended whiskeys) the term "alloy" has become nearly synonymous with mixtures of metals having well defined grain boundaries i.e. with heterogeneous systems. Consequently, when these terms are applied to mixtures of polymers (see Fig. 1) they indicate:

1. polymer blend, PB, a mixture of two or more polymers or copolymers;

2. polymer alloy, PA, a class of polymer blends, heterogeneous in nature, with controlled morphology and properties, achieved by compatibilization.

Polymer blends can be either miscible or immiscible. The miscible blends are divided into homologous (blends of the same polymer, such as a mixture of polystyrene, PS, fractions) and heterogeneous blends e.g. polyphenylene ether, PPE, with polystyrene, PS.

Within the immiscible blends there is a sub-group of compatible polymers. The compatibility indicates commercially valuable blends. To this category belong well-formulated and finely dispersed mixtures of polyolefins, which due to small interfacial tension are morphologically stable. The term "compatible blend" has been misused, to indicate both miscible blends as well as unstabilized, heterogeneous mixtures of immiscible polymers. Note that here the terms: "miscible" and "immiscible" are used in a thermodynamic sense, i.e. miscibility is understood to extend to the intersegmental level.

Consequently polymer alloys must be considered a sub-class of immiscible polymer blends, formed in one of several compatibilization processes. The main reasons for compatibilization are generation and stabilization of optimum morphology to maximize products performance.

By 1986, polymer blends already constituted about one-fifth of the thermoplastics market. They predominate in polyolefins (viz. commercial polypropylene, PP, or linear low density polyethylene, LLDPE) as well as in engineering resins. However, while polyolefins are inherently compatible the engineering blends must be carefully tailored. A summary of polymer alloys and blends, PAB, terminology is given in Table 1.

The history of PAB can be traced to the early years of the rubber industry; Hancock [1] in the first part of the 19th century observed improved performance of natural rubber, mixing it with pitch or gutta percha. In the beginning of this century, with development of synthetic rubbers, blending became an important element of rubber technology [2]. Blending of synthetic thermoplastics is nearly as old as the plastics themselves. For example, polyvinylchloride, PVC, had been known since 1872 but it was the discovery of plasticization that convinced B.F. Goodrich to commercialize it in 1927. Buna-S, (known in the UK as styrene-butadiene rubber, SBR, and in the USA as Government Rubber-S, GRS) was patented in 1933. Shortly afterwards the "permanent plasticizer" effect of the low molecular weight GRS on PVC was noted, leading in 1942 to the first patent on what is today considered a thermoplastic polymer blend [3, 4].

In Table 2 selected thermoplastics blends are chronologically listed by the date of commercialization. The one common feature of the "early" blends has been "partial" miscibility of ingredients. For example, PVC/ABS forms a miscible blend if acrylonitryle content is between 23 and 45% [5]; in PPE/HIPS blends the PPE/PS part is a miscible [6]. The development of polymer alloy is more difficult but due to progress in understanding PAB the time gap between commercialization of a new resin and its blends is being reduced. Sometimes, as a corporate "defensive" strategy, blends are being patented even prior to commercial introduction of a new resin. Since 1980 the introduction rate of PAB has been about four times higher than that of new polymers. From the point of view of processability the miscible blends are preferred, but as fracture mechanics indicates the immiscible, compatibilized ones have an edge as far as mechanical properties are concerned.

Present demands focus on multifunctional PAB's [7]; e.g. in automotive application high modulus, low temperature impact resistance and solvent resistance at reasonable cost are essential. Multifunctionality is being achieved using multicomponent PAB, usually combining several amorphous and semicrystalline polymers in a compatibilized alloy [6]. An example of these new materials is Xenoy, a rubber modified blend of polycarbonate, PC, polyethyleneterephthalate, PET, and/or polybutyleneterephthalate, PBT. The tendency is evident in the patent literature [7].

In this chapter, an outline of the basic understanding of PAB science and technology will be presented. One recurrent theme is morphology. The equilibrium thermodynamics imposes certain structures on immiscible

polymer blends, the dynamics of phase separation leads to other ones, while large strain shear and extensional flows deform these structures. During the processing, due to complexity of deformation fields as well as to the notoriously non-equilibrium character, yet other morphologies may be generated. It is impossible to predict PAB behavior without knowing the morphology and the principles involved in its generation [7-23].

## 2. THERMODYNAMICS OF POLYMER BLENDS

Thermodynamics is a crucial starting point. Miscibility defines the flow behavior and orientational effects, i.e. the performance of the finished article. However, due to a low self-diffusion coefficient for macromolecules the equilibrium is difficult to achieve. Problems associated with producing PAB under non-equilibrium conditions can be severe. During the product lifetime its properties drift toward those at equilibrium. For poorly mixed homogeneous polymer blends this is not as detrimental as for heterogeneous polymer blends where slow annealing may lead to voiding at the interface with severe deterioration of properties.

Not a single theory can predict details of the phase equilibrium in commercially attractive systems. The most difficult parameter to handle is polydispersity - by itself rather difficult to determine. In addition, commercial polymers are seldom chemically pure. Modification of composition provides the desirable flexibility for the manufacturer but at the same time may significantly affect the "compatibility". The polymer/polymer miscibility is determined by a delicate balance of enthalpic and entropic forces, significantly smaller than those observed in solutions of small molecules. In

particular, in PAB the combinatorial entropy term is negligibly small. The polymer/polymer miscibility is primarily due to negative heat of mixing, resulting from specific interactions between the two types of macromolecules.

Another characteristic feature of the PAB phase diagram is the existence of the lower critical solution temperature, LCST; the upper critical solution temperature, UCST, which predominates in the low molecular weight systems is rare.

## 2.1 Basic Relations

At equilibrium the Gibbs free energy is given by [24]:

$$G = H - TS \tag{1}$$

where: H, S and T are enthalpy, entropy and absolute temperature. The free energy, enthalpy or entropy of mixing is defined as a difference:

$$\Delta F_m = F - F_0; \qquad F = G, H, S \tag{2}$$

where F and $F_0$ represent the mixture and pure state respectively. The conditions of miscibility in a binary system can be written in terms of the derivative:

$$D \equiv (\partial^2 \Delta G_m / \partial x_1^2)_{P,T} \tag{3}$$

where $x_i$ is the molar fraction of component i in the mixture and P is the

pressure. For $D > 0$ a homogeneous phase, for $D = 0$ a meta-stable one and for $D < 0$ separated phases are obtained. In Fig. 2 $\Delta G_m$ vs $x_2$ is shown. The $\Delta\mu_i$, the chemical potential of the species i, is defined as:

$$\Delta\mu_i \equiv (\partial\Delta G_m/\partial x_i)_{P,T} \tag{4}$$

In Fig. 3 the phase diagram, T vs composition, for a binary system is schematically represented. The spinodial (broken line) is the boundary line between the phase separated and meta-stable region; the curve is calculated setting $D = 0$. The binodial (solid line) is the boundary between the meta-stable and stable regions, calculated at the condition:

$$\Delta\mu_i' = \Delta\mu_i''; \qquad i = 1, 2...n$$

where the upperscripts refer to the two phases. The spinodial and binodial are joined at the critical points defined by:

$$(\partial^3 G_m/\partial x_i^3)_{P,T} = 0 \tag{5}$$

In Fig. 3 two critical points are shown: the upper critical solution temperature, UCST, observed for most low-molecular-weight solutions, and the lower critical solution temperature, LCST, observed for most polymer blends. There are two reason for this apparent diversity in behavior: (i) for most low molecular weight systems LCST is above boiling point, while for polymer blends UCST is usually below either the melting, $T_m$, or the glass transition, $T_g$,

temperature; (ii) while in solutions the dispersive forces predominate, in miscible polymer mixtures the specific interactions do.

## 2.2 Polymer/polymer miscibility

The above considerations are general. In order to apply them to a given type of system one has to:

1. select an appropriate expression for $\Delta G_m$:

$$\Delta G_m = f(P,T,x_i,\ldots) \tag{6}$$

2. determine the value of the characteristic material parameter(s) in Eq (6)
3. solve Eqs (3)-(5) for Eq (6).

Huggins [25] and Flory [26] derived the relation describing the concentration dependence of the free energy of mixing:

$$\Delta G_m/RTV = \sum(\phi_i/V_i)\ln\phi_i + \sum\chi'_{ij}\phi_i\phi_j \tag{7}$$

where V, $V_i$ are respectively volume of the mixture and molar volume of species i, and $\chi'$ is the binary interaction parameter. To achieve miscibility in a two component system:

$$2\chi_{12} < \left(V_1^{-\frac{1}{2}} + V_2^{-\frac{1}{2}}\right)^2 \tag{8}$$

The first term on the right hand side of Eq (7) expresses the combinatorial entropy of mixing, $\Delta S_c$. In polymer blends $V_i$'s are large and $\Delta S_c$ -

contribution is negligible. The second term was originally identified with Van Laar enthalpy of mixing. Over the years it became recognized that there are two non-combinatorial contributions which enter the second term: energetic and volumetric [27]:

$$X'_{12}RT_1^*/P_1^*V_1^* = X_{12}\ v/P_1^*(v-1) + \tau^2 v/2(4/3-v) \qquad (9)$$

where:

$$1 \leqslant v \equiv (V_1/V_1^*)^{1/3} \leqslant 4/3$$

$$\tau = 1 - T_1^*/T_2^*$$

and $P_1^*$, $V_1^*$ and $T_1^*$ are pressure, volume and temperature reducing parameters of liquid 1. According to Eq (9) the interactions are characterized by two terms: energetic interaction parameter $X_{12}$ and the free volume contribution $\tau^2 \geqslant 0$. $X_{12}$ can be treated as originating from Van Laar term, $X_{12}^L \geqslant 0$, as well as from the specific interactions, $X_{12}^S \leqslant 0$:

$$X_{12} = X_{12}^L + X_{12}^S \qquad (10)$$

The temperature dependence of $X_{12}^L$ (broken curve No. 1), $\tau^2$ (broken curve No. 2) and $X_{12}^S$ (broken curve No. 3) is illustrated in Fig. 4. The resulting temperature dependence of $X'_{12}$ (solid line) intersects twice (Fig. 4a) or once (Fig. 4b) the line defined by Eq (8) for $V_1 = V_2$:

$$X'_{12,c} = 2/V_1 \qquad (8a)$$

It can be seen that LCST occurs only in systems dominated by specific interactions, where contributions from dispersive forces are small, i.e. when $|\chi_{12}^{S}| \gg |\chi_{12}^{L}|$.

The phase equilibrium diagram can be seriously complicated by polydispersity; multi-peak spinodials were reported for oligo(styrene)/ oligo(isoprene) blend by McIntyre et al. [28], and Koningsveld et al. [29-32]. It can be shown that the theories discussed above cannot predict such behavior.

In a purely empirical manner Koningsveld [29] expressed Eq (7) as a power series of volume fraction, $\phi$:

$$\chi_{12}' = \sum_{i=0}^{n} a_i \phi_2^i; \qquad n \geqslant 2 \tag{11}$$

where:

$$a_i = \sum_{j=-1}^{m} a_{ij} T^j; \qquad m \geqslant 1$$

With this modification the multi-peak spinodials can be generated. The modified Huggins theory [33] also predicts such a behavior. In the derivation Huggins assumed concentration and orientation dependent surface interaction parameters. The assumption led to:

$$-\chi_{12}' = \ln [1+k_1(1-\gamma)\phi_2 Q]/\phi_2 + \ln[1+k_2\phi_1 Q]/\phi_1 \tag{12}$$

where $\gamma = 1-s_1/s_2$ ($s_i$ are the interacting segment surfaces), $k_i$ are parameters, and

$$Q = 1/(1-\gamma\phi_2)$$

Koningsveld et al. [31] listed the four factors determining the polymer/polymer miscibility: 1. interacting surface areas of the various types of segments, 2. coil dimensions as a function of temperature, molar mass and concentration, 3. molar mass distribution whether or not in connection with 2, 4. free volume. While the first three elements provide the proper shape of the phase equilibrium diagram, the fourth indicates whether the critical point will be of the LCST or UCST type. However, since miscibility of polymers requires specific interactions and these may alter $\Delta S_m$, one should not consider the free volume to be the sole influence on the type of separation of the phases.

In the original theory of polymer solutions [25,26] $\chi'_{12} \gtrless 0$ was treated as a characteristic, independent of the concentration parameter of the system:

$$\Delta H_m/RTV = \chi'_{12}\phi_1\phi_2 = (\delta_1-\delta_2)^2\phi_1\phi_2 \qquad (13)$$

where $\delta_i \equiv (CED)^{\frac{1}{2}}$ is the solubility parameter given by the cohesive energy density, CED, of substance i [24]. The inadequacy of this assumption is clearly visible in Fig. 4; since for polymer blends $V_i$ in Eq (8a) is very large $\chi'_{12,c} \to 0$ and solubility can be expected only in systems dominated

by specific interactions, i.e. those originally not even considered. The modified theories [27, 33-37] removed the restriction that $\chi'_{12} \geqslant 0$ but still state that $\chi'_{12}$ = const. Only in Huggins [34] and Koningsveld et al. [29-32] the models variation of $\chi'_{12}$ with concentration is implicitly given.

The specific interactions include: hydrogen bonding, donor-acceptor, (Lewis acid-base), ionic, ion-dipole, dipolar and charge transfer type [38-41]. However, they are weak; even for the anion-cation ones the miscibility was observed only for ionic content in excess of 5 mol% [39]. On the other hand, there are close to 400 miscible polymer blends described in the literature [14, 42]. An example of these is given in Table 3. While some specific type interactions can be assigned to several pairs listed in the Table, viz. I - aromatic donor-acceptor pair of $\pi$-$\pi$ bonding, II - hydrogen bonding between C=O and $\alpha$-H, III and IV - hydrogen bonding, and IV - ionic interactions, there are others which are difficult to explain. For instance, there is no good explanation for miscibility between PB and PP when mixtures of low density polyethylene, LDPE, with either high density, HDPE, or linear low density polyethylenes, LLDPE were found to be immiscible [43]. Miscibility of PS/PVME may be postulated as due to the n-$\pi$ donor-acceptor pair, but then immiscibility of PS with other ethers (e.g. PEO) remains unexplained.

A further complication is found considering polymer/copolymer or copolymer/copolymer mixtures. In several cases miscibility is observed only within a narrow range of composition. To explain this Paul [44, 45] and Karasz [46, 47] postulated that interactions between two macromolecules can be

treated as resulting from three types of segment. In the case of AB-copolymer mixed with C-polymer, or AB-copolymer with AC-copolymer this approach is clear. However, the treatment can also be successfully used to explain polymer/polymer miscibility where the intra-molecular interactions are important. The basic idea is that in some homopolymers the polymerization results in residual stresses within the macromolecule. These can be reduced if another homopolymer is mixed in whose interactions allow these stresses to relax. For copolymer AB mixed with polymer C:

$$\chi'_{12} = \chi'_{AC}\phi_A + \chi'_{BC}\phi_B - \chi'_{AB}\phi_A\phi_B \qquad (14)$$

where $\chi'_{ij}$ is the interaction parameter between segments i and j. Note that even if all $\chi'_{ij} > 0$, i.e. there is a repulsive interaction between all three pairs, the overall interaction parameter, $\chi'_{12}$, can be either negative or positive depending on $\phi_i$ and $\chi'_{AB}$, i.e. on the "repulsiveness" between copolymer segments or the magnitude of stresses in homopolymer 1; see Fig. 5. In other words a system can be miscible ($\chi'_{12} < 0$) not only due to specific interactions, but also due to less severe repulsive forces between segments of two polymers than those existing within each of them. Conceptually, Eq (14) provides a good explanation for the miscibility of PVC, PC, polyepichlorohydrin or polyhydroxyether of bisphenol A with linear polyesters in which the concentration of $CH_2$, $\phi_A$, falls within specific limits [45].

## 2.3 Dynamics of Phase Separation

The phase diagram in Fig. 3 allows identification of three systems:

immiscible within spinodials, meta-stable between spinodial and binodial, and miscible on the outside of binodials. In the meta-stable region some activation mechanism must trigger the phase separation. Due to fluctuation of density in the meta-stable region spinodial is diffuse - the need for the activation rapidly vanishes as the conditions move from the binodial toward spinodial. The phase separation phenomena were discussed by Kwei and Wang [48] as well as by Olabisi, Robeson and Shaw [17]. Two types of phase separation were identified: the nucleation and growth, NG, and the spinodial decomposition, SD. Both terms refer to early stages of phase separation prior to diffusion and/or coalescence controlled phase ripening.

The NG takes place after the miscible sample is "shallow quenched" into the meta-stable region. The nucleation is initiated by local fluctuations of density. The required magnitude of the activation energy for nucleation, depends on the value of the interface energy required to create nucleus, i.e. a product of the interfacial tension coefficient, $\nu$, and the surface of the nucleus, S. Following the nucleation the droplet grows by diffusion of macromolecules into the nucleated domains. The rate of this process can be approximated by the relation [49]:

$$dV_d/dt \propto \nu\, x_e V_m D_t/RT \qquad (15)$$

where $V_d$ is the droplet volume, $x_e$ is the equilibrium concentration, $V_m$ is the molar volume of the droplet phase and $D_t$ is the diffusion coefficient.

The phase separation via the NG leads to droplet/matrix structure. Stabilization of the nucleated meta-stable system will determine the size of the droplet at equilibrium but not the morphology. In NG the nucleation depends on the energy or concentration waves. The amplitude of these depends on the distance from the critical conditions. As a consequence, near the spinodial the distinction between the meta-stable and immiscible regions becomes diffused and the phase separation can occur either by the NG mechanism or by the spinodial decomposition [50].

"Deep quenching" leads to SD. To describe the dynamics of phase separation within the immiscible or spinodial domains one considers the balance between thermodynamics and material flux. Cahn and Hilliard [51] solved the dynamic flux equation to the second term. The most interesting is the observation of generality of the SD behavior. For metallic alloys, inorganic glasses, small molecular systems and polymer blends Snyder and Meakin [52-54] reported that $q_m$ is a single parameter function of $\tau$, where $q_m$ and $\tau$ are respectively reduced correlation length and time:

$$q_m = \zeta_0 \beta_m \tag{16}$$

$$\tau = tD_0/\zeta_0^2 \tag{17}$$

with $\beta_m$ the maximum value of the scattering wave vector, t- the quench time, $D_0$ and $\zeta_0$ respectively the diffusion coefficient and the concentration correlation length at the quench time, t=0. Empirically [52]:

$$\ln q_m = -\ln(1+0.05\tau) \qquad (18)$$

The observations are summarized in Fig. 6. Both experimental [55] as well as computational [56, 57] works indicate that phase separation via SD leads to an interpenetrating network. There is a significant volume of literature on extending the linear Cahn and Hilliard [51] theory [58-63]. However, in a recent review Hashimoto proved that linear approximation adequately describes the initial stage of phase separation [64].

The modern theories of polymer dynamics generate the observed NG or SD pattern of phase separation by considering different "quench depth". The unity of the phenomenon on both sides of the spinodial has been emphasized by Leibler [65] and Yerukhimovich [66]. The difference in morphology generated by NG and SD is illustrated in Fig. 7. Further discussion on the subject can be found in [67-80].

## 2.4 Methods for Determination of Miscibility

In the preceding two parts, liquid-liquid miscibility was discussed in terms of equilibrium and non-equilibrium conditions of polymeric mixtures at temperatures above the melting, $T_m$, and/or the glass transition, $T_g$, temperature of all components. As indicated in Fig. 3 the temperature, T (and similarly the pressure, P) may severely change the phase behavior. Thus, miscibility must be considered only within the framework of the experimental range of conditions used during the miscibility test. The predominance of LCST behavior is only statistical and lowering the temperature of a

homogeneous polymer mixture may lead to UCST phase separation.

During processing the formed article is quenched to ambient temperature with a rate dependent on process and thickness of the part. It can be calculated that in injection molding the initial drop of temperature $dT/dt \gtrsim 1000°C/min$. On the other hand, in extrusion of a thick wall pipe the rates $dT/dt \approx 10°/min$ dominate. As a result, morphology of the finished part may be dictated either by that existing in the liquid mixture during processing or by the cooling process. In either case the morphology is not at equilibrium. The situation is more complex if the polymers are semicrystalline. Crystallization changes concentration in the amorphous portion of the blend, which affects phase equilibrium conditions. Furthermore, the presence of the second polymer affects the kinetics and degree of crystallization, i.e. final blend morphology [14, 17, 81].

The Hoffman-Lauritzen kinetic theory of crystallization [82] predicts variation of the melting point of a homopolymer with the interfacial energy, $\nu_e$, heat of fusion, $\Delta H_f$, and lamellar thickness, L:

$$T_{m,0} = T^0_{m,0}(1-2\nu_e/\Delta H_f L) \qquad (19)$$

In multicomponent systems, variation of L has a strong effect on $T_m$. The theory of heat-flux limited crystallization was developed by Illin et al. [83]. Computer modeling of crystallization during injection molding has been successfully treated by Kamal and his collaborators [84-86].

The methods for determination of miscibility in polymer blends can be divided into two groups: I. quantitative, leading either to determination of phase diagram or the polymer/polymer interaction parameter $\chi'_{12}$, and II. qualitative, allowing only estimation of blend miscibility. A summary of the tests is given in Table 4. The first method in category I is based on melting point depression. Considering a homogeneous mixture of polymers from which polymer-1 crystallizes, Nishi and Wang [87] derived the relation between $T_m$ and concentration of polymer-2, $\phi_2$:

$$T_m/T_{m,0} = 1 + \chi'_{12}(RTV_1/\Delta H_f)\phi_2^2 \qquad (20)$$

where $\chi_{12}$ is assumed constant [87-94] (see Fig. 8). Comparing Eqs (19) and (20) it is evident that the latter one is valid only when $dT_{m,0}/d\phi_2 = 0$, i.e. when neither $\nu_e$, $\Delta H_f$ nor L varies with $\phi_2$. In general, $\chi'_{12}$ depends on T, P, $\phi_2$, molecular weight, MW, and molecular weight distribution, MWD:

$$\chi'_{12} = \chi'_{12}(T,P,\phi_2,MW,MWD,\ldots) \qquad (21)$$

From the thermodynamic point of view, crystallization lowers the total free energy of the system expressed as:

$$\Delta G = \Delta G_m + \Delta G_c \phi_c \qquad (22)$$

where $\phi_c$ is the volume fraction of the crystal, $\Delta G_m$ represents the free energy of mixing, and $\Delta G_c$ is change of free energy due to crystallization:

$$\Delta G_c = -\rho_c \Delta H_f \Delta_c / T_m^0 \qquad (23)$$

with $\Delta_c$ representing the supercooling and $\rho_c$ crystal density. Paul and Barlow [95] identified five patterns of crystallinity development upon addition of crystallizable diluent where it: (1) does not affect crystallization, (2) retards crystallization rate, (3) prevents crystallization at high loading, (4) accelerates crystallization, and (5) provides enough thermal mobility to cause crystallization of normally non-crystalline polymer. The coupling between $\Delta G_m$ and $\Delta G_c$ further complicates use of Eq (20) to estimate blend miscibility; to crystallize the systems $\Delta G$ must be negative, or: $T_m \Delta G_m < \rho_c \Delta H_f \Delta_c$.

The second method of estimating miscibility is calorimetric. Since the configurational entropy in Eq (7) is small Paul and Barlow [96-99] proposed a simple calorimetric scan of low molecular weight analogues to predict miscibility of polymers. The value of the parameter $\chi'_{12}$ determined in this "analog calorimetry" method was shown to agree reasonably well with measured values for polymeric pairs. The method is quick, and is easy to use and interpret.

The oldest method of determination phase equilibria is by turbidity measurements. The method consists of preparation of a series of mixtures near phase separation then causing the separation to occur. The onset of turbidity is observed either visually or in a photoelectric cell [17, 24, 100-127]. The ensemble of the turbidity points define the cloud-point curves, CPC. For strictly binary mixtures at equilibrium, CPC should follow the binodial. A

version of the turbidity measurements was proposed by Shaw and Somani [128-133], under the name of the melt titration technique, MTT. This method uses an extruder equipped with a special die, optical detector, traced return tube and a syringe-pump. The test starts with the major component circulating through the system, then the second polymer (in a volatile solvent) is added. The phase separation is detected by an increase in scattered light intensity.

The scattered light intensity at zero scattering angle also allows estimation of the spinodial temperature, $T_S$. However, the method is limited to homogeneous systems. Since the difference between $T_S$ and the binodial temperature, $T_B$, can be as large as 40°C [50] it is desirable to extend the measurements closer to $T_S$. The pulse-induced critical scattering, PICS, does this. The laser light scattering intensity is measured after the thermal equilibrium is reached, but before the system can phase separate, then the mixture is brought out into the homogeneous region and the cycle repeated [134-136]. The temperature change can be accomplished in milliseconds with one cycle time of less than one minute. PICS has been incorporated into a "centrifugal homogenizer" built [137-141] to accelerate the phase separation.

The principle of light scattering can be extended to other sources of radiation, e.g. X-rays and neutrons. In order to be able to follow the fluctuation of density in the sub-micron region, the scattering angle must be small. The small angle X-ray scattering, SAXS, and small angle neutron scattering, SANS, are increasingly used to study polymer blend structure. The methods can be used for liquid, glass or crystalline states. Zin and Roe [116-118] investigated the phase equilibria in systems containing

poly(styrene-b-butadiene) di-block polymer, SB, mixed either with a homopolymer or random copolymer. Plotting the reciprocal of the intensity of the main SAXS peak as a function of 1/T (see Fig. 9) the authors determined the spinodial, $T_S$, and binodal, $T_B$, temperatures. Stein and coworkers [142-145] frequently used SAXS to study the morphology of polymer blends in the solid state.

SANS is one of the most important new tools for studying of macromolecular sizes, conformation and morphology in molten or solid state. For the test, hydrogen must be partially replaced by deuterium. The deuterated polymer is then dissolved in a non-deuterated matrix at a concentration usually below 0.1%. The results are treated similarly to those in classical light scattering. Not only the interaction parameter but also the molecular weight and coil size can be determined. A concise review on SANS application to polymeric systems has been published by Sperling [146] and by Keller [147]. The method has been applied to polymer blends in several recent papers [148-156].

The application of fluorescence techniques to characterize polymer blends has been discussed in the reviews [157, 158]. The term is applied to seven different methods, presented in Table 5. Of these the excitation fluorescence, EF, is the most common [77, 159-168]. In order to measure EF one has to have a system containing excimer, i.e. an electronically excited molecular complex formed from two identical n-systems sharing the same quantum of excitation energy. The excimers are natural aromatic rings, either grafted or dissolved in one polymer of the blend. EF is usually measured on quenched

films using a steady-state illumination method [77].

Several methods discussed allow determination of $\chi'_{12}$: the depression of $T_m$, SAXS, SANS and to same extend the "analog calorimetry" [88]. There are also several indirect methods involving two polymers and a solvent. The first of these methods is based on a Hess cycle, which simply states that the change $\Delta$ in any thermodynamic state function depends only on the initial and final states, not on the path between them. For example, the state function, F, of the blend solution can be calculated either as:

$$\text{I.} \qquad \Delta F(1,2) = \Delta F_m(1) + \Delta F_m(2) + \Delta F(\text{solution}) \tag{24}$$

or:

$$\text{II.} \qquad \Delta F(1,2) = \Delta F(\text{blend}) + \Delta F_m(1+2) \tag{25}$$

In case I, polymers were dissolved separately $(\Delta F_m(1) + \Delta F_m(2))$, then mixed together $(\Delta F(\text{solution}) \to 0)$. In case II, polymers were first blended together $(\Delta F(\text{blend}))$, than dissolved $(\Delta F_m(1+2))$. From Eqs (24) and (25):

$$\Delta F(\text{blend}) = \Delta F_m(1) + \Delta F_m(2) - \Delta F_m(1+2) \tag{26}$$

Usually, in calorimetric studies the enthalpy is being measured, i.e. $\Delta F = \Delta H$. Knowing $\Delta H(\text{blend}) \equiv \Delta H_m$ the enthalpic interaction parameter can be calculated from Eq (13).

The second method of determination of $\chi'_{12}$ in three component systems containing solvent is based on probe vapour sorption (inverse gas chromatography, or IGC). The method is described by Olabisi, Robeson and Shaw [17]. More recently Walsh and McKeon [113] tabulated $\chi'_{12}$ at 120°C for blends containing 50/50 by weight of polyvinylchloride, PVC, either with: polyethyl methacrylate, poly(n-propyl methacrylate), poly(n-butyl methacrylate), poly(n-pentyl acrylate), poly(n-propyl acrylate) or with poly(n-butyl acrylate). DiPaola-Baranyi et al. [169-172] investigated solubility of polystyrene/poly(n-butyl methacrylate) at 140°C in the full range of concentrations. The authors observed significant variation of $\chi'_{12}$ with solvent-probe. Lipatov et al. [173-174] determined $\chi'_{12}$ for cellulose acetobutyrate/polyacetal, PS/PC and HDPE/poly(ethylene-co-vinylacetate). The interaction parameters for chlorinated polyethylene/polyethylmethacrylate [175], polyethylene oxide/PMMA [176] were also measured. In all cases (e.g. see Fig. 10) large $\chi'_{12}$ variations were reported.

Over the years Burns et al. [177-180] have been using gel permeation chromatography, GPC, as a method of determination of binodal compositions in three component systems: solvent/polymer/polymer. GPC with a dual detection system allowed determination of the composition of separated phases at equilibrium, yielding tie-lines, critical points and $\chi'_{12}$.

There is also a large and frequently used group of miscibility tests in which the thermodynamic interaction parameter is not directly involved. Examination of: (i) glass transition temperature, $T_g$, (ii) spectroscopy, (iii) microscopy and (iv) rheology can provide information on miscibility.

The glass transition is related to cooperative segmental motion. Boyer [181] suggested that $T_g$ involves 50 to 100 backbone chain carbon atoms, i.e. a domain with diameter $d_d \approx 2\text{-}3$nm. In agreement with this, Warfield and Hartmann [182] calculated that in glass transition there are 15-30 statistical segments involved. Much larger values, $D_d = 15$ and from 10 to less than 5nm were assigned respectively by Kaplan [183] and by Bair and Warren [184]. The use of $T_g$ in examination of polymer/polymer miscibility is based on the premise that a single $T_g$ indicates that the domain size is below $d_d$, where $2 \lesssim d_d \lesssim 15$ nm. Confirmation of this can be found in several publications on $T_g$ of multiphase systems; e.g., Frisch et al. [185] observed two $T_g$'s in interpenetrating polymer network systems (IPN's) and blends having a domain size of 10-50 nm large.

It is important to recognize that single $T_g$ is not a measure of miscibility but only of the state of dispersion. This was clearly demonstrated in work by Shultz and Young [186] who dissolved polystyrene (PS) and poly(methyl methacrylate) (PMMA) in naphthalene, sublimated the solvent out, and measured $T_g$ of the blends. In the first scan, a single $T_g$ varied linearly with PMMA content, while in the third, as well as subsequent ones, two $T_g$'s, typical for PS and PMMA, were observed. Apparently, in freeze-dried samples PS and PMMA molecules exist in domains smaller than 15 nm. Upon annealing, these domains coarsened resulting in two $T_g$'s.

The correlations between phase equilibria, miscibility under processing conditions, and $T_g$ are elusive. The glass contains the slowly dissipating memories of the previous treatments, viz., mixing and cooling. Since both the

way the blend is prepared and the rate that it is brought to the initial test condition affect the morphologies and stress distribution, different conclusions can be drawn for the same blend. Of the numerous methods for $T_g$ determination the dynamic-mechanical and thermal are most frequently used [187]. The Couchman equation for binary miscible blends [188]:

$$\sum_i w_i \Delta C_{pi} \ln(T_g/T_{gi}) = 0 \quad ; \qquad i = 1,2 \tag{27}$$

can be written as [187]:

$$w_1 \ln(T_g/T_{g1}) + k w_2 \ln(T_g/T_{g2}) = 0 \tag{28}$$

$$k = \Delta C_{p2}/\Delta C_{p1} \tag{29}$$

Eq (28) describes $T_g$ vs $w_i$ dependence rather well. In Eqs (27)-(29) $w_i$, $\Delta C_{pi}$ (at $T_{gi}$) and $T_{gi}$ are respectively weight fraction, heat capacity difference, and glass transition temperature of specimen i. The parameter k is treated as an empirical measure of miscibility: for miscible systems $k \approx 1$, for immiscible $k \lesssim 0.01$, while for systems near the phase separation $k \approx 0.3$ was reported. Note that index i assignment is arbitrary, i.e. since Eq (28) is symmetrical each k has a counterpart $k^* = 1/k$. This is illustrated in Fig. 11. For comparison the experimental plots are shown in Figs. 12-14. The latter figure is of particular interest. Here $T_g$ of the "compatible" blends PVC/NBR was observed to have an unexplained jump of 25°C near 50/50 composition. However, the discontinuity is a necessity of the symmetry principle for the system with $k \approx 2/3$, $k^* = 1/k = 1.5$. From the magnitude of

k the system may be classified as miscible.

There are, however, exceptions to the generality. For strongly interacting miscible blends, blending is associated with a decrease of specific volume:

$$v = (1 + w_1 w_2 K)\ v_1^{w_1} v_2^{w_2} \tag{30}$$

where K is a measure of the interaction. From the point of view of statistical thermodynamics [192] $T_g$ corresponds to the temperature at which, upon cooling, a certain degree of freedom of motion (or a certain part of the free volume) is lost. Equating the volume of glass and liquid at $T_g$ leads to:

$$T_g^{3/2} = (1 + K^* w_1 w_2)^{3/2} (w_1 T_{g1}^{3/2} + w_2 T_{g2}^{3/2}) \tag{31}$$

where K* is a material parameter. In Fig. 15 $T_g$ is plotted vs weight percent of the poly(N-alkyl-3-hydroxymethyl carbozoylyl methacrylate), n=1 or 2, blended with poly(β-hydroxyethyl-3,5-dinitro benzoyl methacrylate) [193]. The polymers form strong electron-donor-acceptor, EDA, miscible complexes with single $T_g$'s. Lowering of K* upon increasing length of the alkyl group is to be noted.

Information on miscibility can be gleaned not only from $T_g$ vs $w_2$ dependence but also from the width of the transition, TW. While for neat

polymers TW ≈ 6°C, for miscible and immiscible blends TW = 10 and 32°C, respectively [189]. Alexandrovich [194] reported that in miscible blends TW depends on composition and method of blend preparation. TW may provide information on miscibility in difficult cases where due to closeness of the glass transition temperatures, $|T_{g1}-T_{g2}| \lesssim 10°C$, there are difficulties in ascertaining miscibility on the basis of $T_g$ vs $w_2$ plot. This approach is particularly suitable for $T_g$ determination by dynamic-mechanical methods.

Within the spectroscopic tests of PB-miscibility the nuclear magnetic resonance, NMR, and infrared, IR, methods are the most important. The early papers on application of NMR methods were reviewed by Olabisi et al. [17] and by Robeson [42], the more recent ones in [195-208]. The parameters used in determination of polymer/polymer miscibility are the half-life of the spin relaxation times: the spin-lattice, $T_1$, the spin-spin, $T_2$, and the spin-lattice in the rotating frame, $T_{1\rho}$.

The papers by Djordjevic and Porter [209, 210] as well as that of Garton, Cousin and Prud'homme [211-213] are particularly valuable toward determining the molecular source of specific interactions.

Application of infrared spectroscopy, IR, in characterization of polymer blends is extensive. There are hundreds of papers on the subject. A review of early works can be found in [17, 42]. Excellent introductions to IR and various spectroscopic methods for polymeric systems have been recently published [214, 215].

The Fourrier transfer IR, FTIR, was used by Coleman et al. [216-222] to study the interactions in blends of polyesters with chlorinated polymers. A similar problem has been tackled by the Canadian team: Prud'homme [223], Garton et al. [211, 224], Cousin et al. [211, 213] and by others [92, 225, 226]. Blends containing PPE were extensively studied [227-229], as well as those of: PC [230-232], Phenoxy [233-236], PS [237-241] and many other polymers [242-249]. The other spectroscopic techniques such as: Brillouin scattering [250], photoacoustic [247] and Raman [240, 251] spectroscopy have seldom been used. The primary application of these has been to study the heterogeneities in polymer blends, viz. crystallization or phase separation.

The microscopy is not so much a method to study miscibility as rather to determine a degree of dispersion in immiscible blends. Operationally, a system is considered miscible if one equilibrium $T_g$, is observed, i.e. when domain size $d < 12nm$. This reduces the variety of microscopic methods to two: transmission, TEM, and advanced scanning electron miscroscopy, SEM. Preparation of samples for observation under TEM is exacting. The specimens have to be hardened, stained, microtomed, mounted on a grid polymeric film support and measured. The surface morphology can be observed under TEM by cryogenic shadow casting and replication methods. The microscopic methods are usually used parallel to one another, the SEM/TEM pair being the most frequent [252, 253]. In all cases microscopy is considered as just one of several methods of characterization of polymer blends [254-256].

There are numerous sources of possible error and introduction of artifacts into the electron microscopy. In particular, metallization in SEM

and $OsO_4$ staining in TEM may introduce an artificial grain structure observed under greater magnification. Serious errors can be made in cases where the size of the deposit and the expected domain size are comparable [257]. Hardening is another source of artifacts. Here, the experience with biological specimens or with emulsions can be of particular value [258].

The last methods to be mentioned for studying miscibility of PB are based on rheological tests. The miscibilities below $T_m$ and/or $T_g$ are easy to ascertain by viscoelastic temperature scan accross these transitions [259-261]. However, for the processor it is at least as important to know if the blend is miscible in the molten state. The studies of the flow behavior of polymer blends can provide this information. Since the melt flow of PAB will be reviewed in the following part, these methods will be discussed later.

## 2.5 Compatibilization

The variation of morphology with processing conditions and the phase ripening due to aging are two characteristics of heterogeneous blends which inhibit a wider penetration of blends into the market. Both the resin manufacturer and the processor, are looking for a material, which can tolerate process variability, handling, and storing. One obvious solution is to look for miscible blends. However, not only are these rare, but they also require impact modification [262-270]. As a result, the aim is to produce heterogeneous blends which will be as easy to handle and as stable and reproducible as homopolymers. The way to obtain these is by stabilization of the phases via "compatibilization" or alloying.

The compatibilization methods can be divided into three categories loosely labeled: mechanical, physical and chemical. The aim of mechanical compatibilization, MC, is development of a non-equilibrium morphology which in one respect is relatively stable and reproducible yet in another respect leads to enhancement of properties. "Mechanical locking" in 50:50 PE/PS blend resulted in morphology that was stable for at least 3 hrs at 180°C [271]. The authors used the "Maxwell normal stress extruder". It seems that MC is particularly suitable near the phase inversion region. Recently Jordhamo, Manson and Sperling [272] reported that this takes place when:

$$\phi_1/\phi_2 = \eta_1/\eta_2 \equiv \lambda \qquad (32)$$

($\phi_i$ and $\eta_i$ is the volume fraction and shear viscosity of component $i = 1,2$ in the blend). However, not all PB's seem to follow this rule. The other MC method is mixing micronized powders or latexes in processes where neither phase ripening nor large coalescing strains occur; e.g. rotomolding of impact modified blends, or preparation of ABS by latex blending.

The physical compatibilization, PhC, is best known [14, 17]. To this category belong: (i) modification of polymeric structure to enhance miscibility, e.g. by introduction of ionic or hydrogen bonding groups, (ii) control of crystallization as a means to lock-in developed morphology, and (iii) addition of compatibilizing agents. The miscibility enhancement via introduction of interacting groups, e.g. anions into polymer-1 and cations into polymer-2 was discussed in part 2.2. The use of crystallization to prevent blend coarsening has been reviewed in the subject literature cited in

part 2.4. The addition of compatibilizer is by far the most popular method of alloying.

The most frequently used compatibilizers are: block copolymers, graft copolymers, co-solvents or interacting copolymers. The theory of compatibilization by addition of di-block polymers has been developed by Noolandi and Hong [273-275]. The A-B block copolymer was assumed to selectively dissolve, block A in polymer-A and block-B in polymer-B, binding the two A and B phases via chemical bonds. It was expected that upon addition of block copolymer the interfacial tension and the size of the dispersed phase will decrease and the thickness of the interphase layer will increase, creating material with macroscopically homogeneous behavior. The best examples can be found in work from the University of Liege [276-292]. In a series of carefully designed experiments the authors demonstrated that the best results are obtained using A-B block polymers with "tapered" structure, i.e. with a central part where composition gradually changed from A to B. As an example, LDPE/PS blends were compatibilized by addition of tapered block copolymer of the type: hydrogenated polybutadiene (HPB) - random copolymer HPB/PS - polystyrene (PS). Optimization of the compatibilizer MW and structure requires "painstaking feedback cycles between synthesis and evaluation". Since block copolymers are expensive, optimization involves methods of blend preparation designed to place the compatibilizer only on the interface; usually at least 2 to 5% is required.

There is an extensive literature on compatibilization [14, 17, 293-300]. Historically, graft and multiblock copolymers have been more frequently used.

To compatibilize with block copolymer it is sufficient that block A dissolves in one phase whereas block B dissolves in another. For example poly(caprolactone-b-styrene) or poly(methylmethacrylate-b-styrene) can be used to compatibilize PVC/PS blends, poly(hydrogenated butadiene-b-methylmethacrylate) to enhance properly of Kraton-G/PVC [292], etc.

The big-volume manufacturers tend to rely on addition of large amounts of non-optimized multicomponent copolymers. As the patent literature indicates, new copolymers introduced on the market are being immediately explored for their compatibilizing capability [301, 302]. Sometimes addition of a copolymer may have an unexpectedly large effect. In a recent patent [303] it was demonstrated that addition to PBT of either PC or SAN/EPDM graft copolymer has only a small effect on impact strength, but when the three components were combined (20% SAN-copolymer) a tenfold improvement was obtained.

Another compatibilization method bridges the gap between physical interactions and chemical bonding. To this group belong polymer modifiers like maleated polyolefins, ionomers, "metalated" polymers [304] and others. Compatibilization of PP/PA blends by addition of maleated-PP is probably accomplished without formation of covalent bonds between amide and maleic anhydride groups. Compatibilization via ion-dipole interaction also occurs without such bond formation [38, 39]. "Metalation" of poly(p-phenylene terephthalamide), PPTA, in effect generated polyanion which then interacted with PVC to form molecular composite structure with PPTA microfibrils of about 20-40 nm diameter.

The last category of compatibilization methods is chemical compatibilization or CC. Here the chemical reaction is essential as in: (i) formation of the interpenetrating polymer network, IPN, or semi-interpenetrating network, SIN [185, 305-315]; (ii) either reversible or permanent crosslinking/vulcanization [2, 38, 316-320]; (iii) exchange reaction creating "in situ" the compatibilizing copolymer [321-326], (iv) reactive processing [327-332], etc. Compatibilization via IPN and reactive processing are developing into individual branches of polymer science and technology. In CC permanency of the structures may prevent recycling and increase the cost.

## 2.6. Thermodynamically imposed structures

The equilibrium thermodynamics predicts the temperature and concentration of phase separation, but not the size or shape of the separated phase. In principle, by introducing the interfacial energy and assuming regularity of structure one can predict how PAB morphology will change with $\phi$ and T. Experimental verification of these calculations is difficult. MWD, non-uniform blend history and low diffusion rates cause serious problems; the variability of the interfacial energy engendered by commercial additives also leads to irreproducibility of results.

However, studying block polymer behavior, one can learn what equilibrium morphology is to be expected. There is a vast literature on the subject [333]. Both theory and experiments indicate that the form of the separated phases depends (at T,P = const) on composition, whereas their size depends on molecular weight. For volume fractions $\phi < 0.12$ droplets, for $0.12 \lesssim \phi \lesssim 0.38$ cylinders, and for $0.38 < \phi < 0.62$ lamellas are formed [334]. In PAB, as in

classical emulsions, the size of the dispersed phase depends primarily on the interfacial tension, $\nu$ [273-275, 335-342].

As indicated in part 2.3 the dynamics of phase separation may result in micro-droplets (NG) or interconnected structure (SD). These non-equilibrium morphologies will tend toward those determined by equilibrium thermodynamics, initially via interface diffusion process, where d is a function of the coarsening time [55]:

$$d \propto t^{\ell} \qquad (33)$$

where $\ell$ is a parameter. At the earliest stages of coarsening $\ell = 1$, whereas in the intermediate $\ell = 1/3$ ("Ostwald ripening" via coalescence of spherical droplets, or constant volume "evaporation" [343]).

The morphologies discussed so far refer to melts in which the process - imposed deformations are absent. By chemical (e.g. crosslinking) or physical means (e.g. crystallization) it is possible to "freeze" the non-equilibrium structures imposed either by the dynamics of phase separation or by flow. These structures can be significantly different from the ones discussed above.

## 3. MELT FLOW OF POLYMER BLENDS

Polymer rheology has been widely investigated both in its fundamental [344-360] as well as experimental [361-373] aspects. However, studies of multiphase flow are relatively recent [368, 374-375]. The term "multiphase"

refers to liquid systems containing either gas (foams), solid (suspensions, composites) or liquid (emulsions, blends or stratified flow). While here only blend flows will be discussed, in several cases the rheological behavior of PAB is easier to understand considering other systems, e.g. suspensions or emulsions. In the text the nomenclature adopted by the Society of Rheology [376] will be used.

## 3.1 Basic relations

Three types of flow are of interest: (i) steady state shear, (ii) dynamic or oscillatory shear, and (iii) uniaxial extensional flow.

Re. (i). After imposition of a rate of shear, $\dot{\gamma} = \dot{\gamma}_{12}$, the response is registered in a form of stress tensor whose components are $\sigma_{ij}$, where i,j = 1, 2, 3 indicate the orthogonal planes indices. The shear viscosity, $\eta$, the first and the second normal stresses, $N_1$ and $N_2$, as well as their coefficients, $\Psi_1$ and $\Psi_2$, are defined as:

$$\eta = \sigma_{12} \dot{\gamma} \tag{34}$$

$$N_1 = \sigma_{11} - \sigma_{12} ; \quad \Psi_1 = N_1 / \dot{\gamma}^2 \tag{35}$$

$$N_1 = \sigma_{22} - \sigma_{33} ; \quad \Psi_2 = N_2 / \dot{\gamma}^2 \tag{36}$$

Re. (ii). When a liquid undergoes sinusoidal deformation with frequency $\omega$ the response is expressed in terms of in-phase or storage, G', and 90°

out-of-phase of loss, G", moduli. The complex modulus is given by:

$$G^* = (G'^2 + G''^2)^{\frac{1}{2}} \tag{37}$$

Correspondingly the three functions can be defined:

$$\eta' = G''/\omega \; ; \qquad \eta'' = G'/\omega \; ; \qquad \eta^* = G^*/\omega \tag{38}$$

called respectively dynamic, out-of-phase, and complex viscosity.

Re. (iii). The strain and the elongational rate of straining are defined as:

$$\varepsilon = \ln L/L_0 \; ; \qquad \dot{\varepsilon} = d\,\varepsilon/dt = d\ln L/dt \tag{39}$$

where $L_0$ and L are initial and after time, t, length of the specimen. The stress growth function and its equilibrium value are defined as:

$$\eta_E^+ = \sigma_{11}^+/\dot{\varepsilon} \; ; \qquad \eta_E(\dot{\varepsilon}) = \lim_{t\to\infty} \eta_E^+(\dot{\varepsilon}) \tag{40}$$

At very low deformation rate, $\dot{\gamma} = \omega = \dot{\varepsilon} \to 0$, the single phase neat liquids (without yield stress) behave as Newtonian:

$$\eta_0 = \lim_{\dot{\gamma}\to 0} \eta = \lim_{\omega\to 0} \eta' = \lim_{\dot{\varepsilon}\to 0} \eta_E/3 \tag{41}$$

$$N_{1,0} = N_{2,0} = G_0' = 0 \tag{42}$$

where the subscript "o" indicates zero deformation rate.

For liquids with a structure due to: association (e.g. hydrogen bonding), temporary crosslinking (e.g. in PLC or block polymers), by addition of solid particles or by dispersing another liquid, the yield stress, $\sigma_y$, is to be expected. In this case the measured stresses are augmented by $\sigma_y$, which in principle is a constant, characteristic parameter of the system. Here Eqs (41) and (42) are not obeyed.

Outside the range of infinitely small deformation rates most polymeric liquids show non-Newtonian behavior. The term refers to either time, t, or rate of deformation dependencies. If the sheared system shows increase of $\eta$ with t it is called thixotropic. If there is a decrease it is either anti-thixotropic or rheopectic. Historically, the terms referred to non-elastic liquids, e.g. suspensions or emulsions in low molecular weight medium [377-383]. The simplest, single-exponential thixotropic relation is:

$$\eta - \eta_\infty^t = (\eta_0^t - \eta_\infty^t) \exp\{-t/\tau^*\} \qquad (43)$$

where $\eta_0^t$ and $\eta_\infty^t$ refer to initial and final values of viscosity, t is the shearing time, and $\tau^*$ the relaxation time, dependent on $\phi$, T, and $\dot{\gamma}$.

The non-Newtonian system whose $\eta$ increases with $\dot{\gamma}$ are called dilatant (or shear thickening) and when decreases pseudoplastic (or shear thinning) [374,375]. The dilatancy is rare, limited to multiphase systems with rigid

domains, usually at high volume fraction, $\phi$. Pseudoplasticity is dominant in all polymeric systems. Recently, a new relation was proposed [384]:

$$\eta = \eta_0 \left[1 + (\tau^* \dot{\gamma})^{m_1}\right]^{-m_2} \tag{44}$$

where $\eta_0$ is the zero-shear viscosity, $\tau^*$ the primary relaxation time, and $m_1$ and $m_2$ are adjustable parameters. The dependence was tested using data for neat polymers as well as for miscible and immiscible blends [43, 260, 385, 386]. For large $\dot{\gamma}$ Eq (44) can be cast in the form of the " power law" relation:

$$\sigma_{12} \propto \dot{\gamma}^n \tag{45}$$

with the "power law" exponent $n = 1 - m_1 m_2$.

## 3.2 Influence of miscibility on low-deformation rate flow behavior (composition dependence)

In section 3.1 the basic rheological dependencies for liquids were presented. Now the simplest flow behavior at zero-deformation rate (Newtonian) limit for miscible and immiscible PAB will be discussed. Under the isothermal and isobaric conditions, T,P = const, the most interesting dependence is that of $\eta_0$ vs $\phi$. It is convenient to discuss it in terms of the log-additivity rule:

$$\log \eta_0 = \sum w_i \log \eta_{0i} \tag{46}$$

where $\eta_0$, $\eta_{0i}$ are zero-shear viscosities of the blend and its components i, respectively, and $w_i$ is the weight fraction of component i. Blends with $\eta_0$ larger or smaller than predicted by Eq (46) are called, respectively, positively deviating blends, PDB, and negatively deviating blends, NDB [374, 375, 387-390].

3.2.1 Miscible blends can be modeled either by binary solution of two low molecular weight liquids, or a mixture of two homopolymer fractions, i.e. homologous polymer blends. For solutions [391, 392]:

$$\log (V\eta_0) = \sum_i x_i \log (V_i \eta_{oi}) + \log (V\eta_0)^E \qquad (47)$$

where V is the specific volume, $x_i$ is the mole fraction and the "excess" term can be written as:

$$\log (V\eta_0)^E = -\pi \sum_i x_i \Delta H_m / 2.45\ RT \qquad (48)$$

Eqs (47) and (48) predict the "mirror dependence": PBD for systems with the heat of mixing $\Delta H_m < 0$ while NDB, for ones with $\Delta H_m > 0$. Since for miscible blends $\Delta H_m < 0$ (see section 2.2) the solution model predicts PDB behavior for miscible PB's.

For homologous blends with weight average molecular weights larger than the entanglement value, $M_{wi} > M_e$ [393-395]:

$$\eta_{oi} = KM_{wi}^{a} \qquad (49)$$

But $M_w = \sum w_i M_{wi}$; substituting this dependence into Eq (49) and assuming that a and K are independent of polydispersity again PDB behavior is predicted. Similarly, PDB deviation can be computed from the $\eta$-dependence on the free volume fraction, f, derived from the statistical thermodynamic equation of state [396-407].

In short, all the model systems of miscible blends favor the PDB behavior. The experimental observations indicate that indeed PDB predominates, but it is not an absolute rule [43, 385, 408-414]. It seems that the most plausible explanation for NDB [409, 411] is dilatation caused by intramolecular stress relaxation, which leads to increased f and reduced $\eta_0$.

Near the critical conditions for phase separation there is enhanced density fluctuation and the volume of the flow element [391] increases. This results in a local increase of $\eta_0$ [415, 416].

3.2.2 Immiscible blends.

3.2.2.1 Model Systems. Here suspensions, emulsions and block copolymers can serve as models. Viscosities of these systems are expressed in terms of relative viscosity, $\eta_r$, defined as a ratio of suspension or emulsion

viscosity to that of medium. The hydrodynamic volume of the suspended particle or droplet is proportional to the intrinsic viscosity:

$$[\eta] \equiv \lim_{\phi \to 0} (\eta_r - 1)/\phi \tag{50}$$

There is a multitude of proposed relations between $\eta_r$ and $\phi$ for the monodisperse hard spheres suspensions. Out of these, the following two [417, 418] were found to provide the best description [419]:

$$\eta_r = 1 + [\eta]_s \lambda \phi \tag{51}$$

with $$\lambda = 4(1 - Y^7)/[4(1 + Y^{10}) - 25Y^3(1 + Y^4) + 42Y^5]$$

and $$Y = [2(\phi_m/\phi)^{1/3} - 1]^{-1}$$

$$\ln \eta_r = [\eta]_s \phi/(1 - \phi/\phi_m) \tag{52}$$

In Eqs (51) and (52), $[\eta]_s$ indicates intrinsic viscosity of hard spheres and $\phi_m$ is the maximum packing volume fraction. The semi-empirical Mooney's Eq (52) can be derived from the free volume theory [420, 421]. In Fig. 16 the dependencies predicted by these relations are compared with the experimental data [422]: $[\eta]_s = 2.5$, $\phi_m = 0.78$ and $[\eta]_s = 2.5$, $\phi_m = 0.91$ were respectively used in Eq (51) and Eq (52).

The effect of polydispersity of spheres diameter can easily be accounted

for by considering its effect on $\phi_m$ [375]. For example, random packing of binary spheres with diameter ratio varying from 1 (monodisperse) to 20 results in an increase of $\phi_m$ from 0.626 to 0.859. Substituting these values into Eq (51) at $\phi = 0.6$ gives $\eta_r$ = 11,000 and 31.6, respectively. Theoretical predictions for real systems with four or five generations of spheres give $\phi_m \lesssim 0.94$.

The flow properties are also affected by the particle shape. Defining the aspect ratio $p = a_{max}/a_{min}$ ($a_{max}$ and $a_{min}$ being the maximum and minimum particle dimension) the $[\eta]_s$ and $\phi_m$ can empirically be expressed as:

$$Y = [\eta]_s, \phi_m = a_0 + a_1 p^{a_2} \tag{53}$$

where $a_i$ are parameters whose experimental values for discs and rods are listed in Table 6. Once the particle shape and aspect ratio are known, $\eta_r$ can be calculated from Eqs (51) and (53). However, these Equations are valid only in dilute region, $\phi \lesssim p^{-2}$, where free tumbling of anisometric particles is possible. In the semi-concentrated region, $p^{-2} < \phi < p^{-1}$, movements take place in two-dimensions. Rheologically this results in a decrease of the apparent hydrodynamic volume of the particles, observed as a decrease in the rate with which $\eta_r$ increases with $\phi$ [425].

It has been proposed [426] that the effect of crowding on $[\eta]_s$ be

considered as similar in its limit to that induced by high strain rates. for rods [427]:

$$[\eta]_0/[\eta]_\infty = p/1.17 \qquad (54)$$

where subscripts "0" and "∞" indicate limits: $\dot{\gamma} \to 0$ and $\dot{\gamma} \to \infty$, respectively. For discs the numerical factor of 1.17 ought to be changed to 3.31. Doi and Edwards predicted that for rods $\eta_r \propto \phi^3$ [428].

The third complicating aspect of Newtonian suspensions is particle association leading to formation of aggregates. Aggregation, agglomeration and flocculation are structural phenomena ranging from transient rotating doublets [429] to pseudo solid-like behavior of flocculated suspensions with yield [430-436]. The aggregation can be due to interparticle thermodynamic interactions, chemical bonding or crowding in simple geometric terms. The latter type prevails in shear flows.

There are several theories based on structural models out of which that recently developed by Wildemuth and Williams [434] is particularly interesting. Assuming that the structure depends on $\sigma_{12}$ and defining $\phi_{m,0}$ and $\phi_{m,\infty}$ as the values of $\phi_m$ at normalized shear stress $\sigma_{12} \to 0$ and $\sigma_{12} \to \infty$, respectively, the authors derived the relation:

$$\phi_m = (\phi_{m,0} + \phi_{m,\infty}\sigma_{12}^m)/(1 + \sigma_{12}^m) \qquad (55)$$

where the experimental constant m = 1.00 to 1.17. Eq (55) can be used to predict the yield stress value of, $\sigma_y$, if m, $\phi_{m,0}$ and $\phi_{m,\infty}$ are known:

$$\tilde{\sigma}_y = (\phi - \phi_{m,0})/(\phi_{m,\infty} - \phi) \tag{56}$$

The reduced shear stress:

$$\tilde{\sigma}_{12} = \sigma_{12}/M \tag{57}$$

(M is the fourth parameter of the theory) normalizes the flocculation process in terms of the stress sensitivity.

Similarly, the uniaxial extensional flow of Newtonian suspensions (Troutonian flow) can be treated. The extensional field is irrotational and under steady state flow the particles remain oriented in the direction of stress. Batchelor derived the following relation for dilute suspensions of rods with aspect ratio, p, in Newtonian liquid [437]:

$$n^0_{E,r} = 3 + 4\phi p^2/3\ln(\pi/\phi) \tag{58}$$

where $n_{E,r} = n^0/n_{0,E}$ is the relative extensional viscosity within the Troutonian range of extensional rates, $\dot{\varepsilon} \to 0$. For $\phi \to 0$ the Trouton ratio:

$$R^0_T = \lim_{\dot{\gamma},\, \dot{\varepsilon} \to 0} n_E/3n \tag{59}$$

is unity. For suspensions $R_T^0$ strongly depends on p: at modest concentration, $\phi = 0.4$, Eq (58) predicts $R_T^0 = 1.09$ and 8,627 for p = 1 (spheres) and p = 100 (short fibers), respectively. These predictions have been experimentally verified [438-440]. Even for concentrated suspensions with $\phi > 1/p$ a reasonable agreement was obtained [375].

Both theory (in which Brownian motion is considered) and experiment indicate appearance of elastic effects on shearing suspensions of anisometric particles in Newtonian medium [441-445]. There are also orientational and morphological changes (viz. migration of particles to center of stream in a pipeflow), leading to plug (Bingham) flow and other non-Newtonian effects. Interested readers should consult [375].

The two components in PAB can be characterized by the ratio of their rheological functions; viz. Eq (32):

$$\lambda = \eta_1/\eta_2 \; ; \qquad \lambda_E = \eta_{E1}/\eta_{E2} \; ; \qquad \lambda_N = N_{1,1}/N_{1,2} \tag{60}$$

with index 1 and 2 indicating dispersed and matrix liquid, respectively. Suspensions can be considered one limiting model system in which $\lambda = \lambda_E \to \infty$, emulsions the other in which $\lambda = 1$.

The intrinsic viscosity of emulsions, $[\eta]_E$, was expressed by Oldroyd [446] as:

$$[\eta]_E = 2.5\ (\Lambda + 2/5)/(\Lambda + 1); \qquad \Lambda = (\eta_1 + \eta_i/5d)/\eta_2 \qquad (61)$$

where $\eta_i = 2\eta_{si} + 3\eta_{ei}$ expresses the shear, $\eta_{si}$, and extensional, $\eta_{ei}$, viscosities of the interface and d is droplet diameter. Eq (61) is valid in a dilute region. It is worth noting that for $\Lambda \to \infty$, in accord with Einstein's prediction for hard spheres suspensions, $[\eta]_E = 2.5$. Equation (61) was verified experimentally for $\Lambda \gtrsim 1$ [447].

In the dilute region, Eqs (51) and (52) can be used for emulsions with $[\eta]_E$ calculated from Eq (61), treating $\phi_m$ as a parameter that depends on the interphase [448, 449]. Note that increase of $\eta_r$ is predicted for both emulsions: A and B and B in A, i.e. PDB may be expected for random liquid mixtures.

As the concentration increases there is a tendency for droplets to aggregate [430,450-452]. Commercial emulsions with $\phi \lesssim 0.99$ have been prepared. These highly concentrated systems bear more resemblance to elastic solids than liquids.

The last system which may serve as a model of immiscible PAB is block copolymer. Several excellent books and reviews describe the behavior of these materials [453-457]. The amorphous block copolymers of the type styrene-butadiene-styrene, SBS, are characterized by two glass transition

temperatures, $T_{gB}$ and $T_{gS}$, as well as the separation temperature, $T_s$ [458-470]. At $T > T_s$ the copolymer forms a single phase, at $T_{gS} < T < T_s$ the two chemically different blocks coexists as separate but linked liquid phases. The viscosity of the system is much higher than predicted from $\phi$ and MW values [458-464]. As Williams et al. [465, 466] indicated, the reason for this is deformation of domains and pulling filaments of one polymer through domains of the other. Viscosity increases with incompatibility of the components. This behavior leads to apparent yield stress and non-Newtonian behavior [467-470]. At $T_{gS} < T < T_s$ SBS can be homogenized if the shear stress $\sigma_{12} > \sigma_c$ where [471]:

$$\sigma_c^2 = a_0\, T(T_s/T - 1)\ ; \qquad T \lesssim T_s \tag{62}$$

with $a_0$ being material parameter. Recently, a similar phenomenon was reported for SAN/PMMA blends [472]. The authors observed NG or SD mechanism of phase separation, depending on the quench history.

3.2.2.2 Newtonian behavior of immiscible blends and alloys

It is useful to separate immiscible blends into two categories: (i) immiscible in the whole range of composition, and (ii) those with miscibility at low concentration. The flow behavior of (i) can be modelled using suspensions ($\lambda \gg 1$), emulsions ($\lambda = 1$) or block polymeres as examples. To understand the flow behavior of (ii) examples must be taken from miscible systems (part 3.2.1), flow near the critical conditions, and that of immiscible blends.

Due to high viscosity of commercial polymer melts, and the apparent yield phenomenon near the inversion concentration, $n_0$ of PAB is rarely reported. Instead, $\eta$ at constant $\dot{\gamma}$ or at constant $\sigma_{12}$ are being measured. Since, at the interface $\dot{\gamma}$ is discontinuous but for most systems $\sigma_{12}$ is a continuous function, there are recommendations for the latter condition to be used [368]. Statistically, about 60% of PAB shows PDB, 30% NDB and the remaining 10% a mixed Positive-Negative Deviating Blend, PNDB behavior [388]. The classification of PAB based on the deviation from log-additivity is pertinent to the flow mechanism, but not necessarily to the chemical nature of blends; changing the molecular weight or test temperature may significantly alter the flow mechanism and the type of deviation from the log-additivity rule [473, 474]. For example, blends of PS/PE [474], POM/Copolyamide [475, 476], Polyamide-6 (PA-6)/PE [477], HDPE/LDPE [478, 479] show PDB deviation, those of HDPE/PA-6 [480], PS/PE, PS/PP [481, 482], Polyethyleneterephthalate (PET)/PA-6 [483], PS/POM, PA-12/PMMA [484] LDPE/POM and PS/polycarbonate (PC) [485, 486] show NDB, whereas blends of cis-polybutadiene (PBD)/cis-polyisoprene (PIP) [487], LDPE/PP [488], cellulose acetate butyrate (CAB)/POM [489, 490], PMMA/POM [484] or PET/PA-6,6 [388] show PNDB behavior.

Several mechanisms (expected on the basis of the model systems) can lead to PDB; dilatations in miscible blends was the only one which could explain NDB. In immiscible blends, if dilatation occurs it must do so at the interface, i.e. it may be be expected in systems which show "antagonistic" interactions toward each other. The examples listed above are in qualitative agreement with this picture. Furthermore, increasing MW of a component or decreasing T frequently either lead to NDB or deepens that deviation. The

dilatation at the interface may result in an interlayer slip, i.e. a discontinuity of both $\dot{\gamma}$ and $\sigma_{12}$. Lin [491], assuming interlayer slip in the telescopic flow of PAB through a tube, derived the following dependence:

$$1/n = \beta_1[w_1/n_1 + w_2/n_2]; \qquad \beta_1 = 1 - (\beta_{12}/\sigma_{12})\,(\pi w_1 w_2)^{\frac{1}{2}} \tag{63}$$

where $\beta_1$ is the interlayer slip factor, $w_i$ is weight fraction of polymer $i = 1,2$ and $\beta_{12} < 0$ is the characteristic slip factor. Eqs (63), (64) formally allow prediction of NDB behavior.

There are two possible explanations for PNDB: partial miscibility at low concentration, and concentration dependent change of the flow mechanism in the immiscible region. In the miscible region Eyring's "mirror image" can be expected: when $\Delta H_m$ decreases the excess viscosity, $\eta^E$, should increase and vice versa. When critical concentration is approached, the viscosity is expected to increase sharply <u>before</u> the phase separation occurs. When the concentration exceeds the critical value the two-phase flow becomes controlled by structure: $\eta$ will increase further if a dispersion with rigid ellipsoids is created; it will stabilize for an emulsion-type system or decrease for lamellar morphology with interlayer slip. For immiscible systems the relation between $\Delta G_m$ and $\eta^E$ does not exist. Furthermore, the conditions for phase separation in flowing systems differ from those considered by equilibrium thermodynamics (e.g. see Eq (62) [471, 472]). The thermodynamic argument can be used as a qualitative tool to explain concentration dependence of the rheological function at vanishing deformation rates, but not as a quantitative

predicting tool. An example is presented in Fig. 17.

This concludes the discussion on PAB flow under low deformation rates in a Newtonian or near-Newtonian region. Since morphology is strain-dependent, the non-Newtonian flows are divided into small (dynamic) and large strain (steady state shear and extensional) flows to be discussed respectively in parts 3.3 and 3.4.

## 3.3. Small strain flow behavior

Here the yield phenomena, the structural and time effects observed in low strain flows will be summarized.

3.3.1 Yield stress is that stress value below which no flow can be observed under the experimental conditions (e.g. see parts 3.1, 3.2.2). Experimentally, it can be determined using the modified Casson equation [493]:

$$F^{\frac{1}{2}} = F_y^{\frac{1}{2}} + aF_m^{\frac{1}{2}} \qquad (65)$$

where F may stand for shear stress, $\sigma_{12}$, elongational stress, $\sigma_{11}$, shear loss modulus, G", etc. $F_y$ indicates the yield value of F, $F_m$ is the F-value of the matrix at the same deformation rate as F and a is a measure of the relative value of F. For instance, if $F = \sigma_{12}$ then $F_y$ is the yield stress in shear, $\sigma_y$, and $a^2 = \eta_r$. The concentration dependence of $\sigma_y$ can either be expressed as [493]:

$$\sigma_y = K(\phi - \phi_0)^n \tag{66}$$

or [423]:

$$\sigma_y = A_1 \exp\{A_2 \phi\} \tag{67}$$

In these relations K, $\phi_0$, n, $A_1$ and $A_2$ are adjustable parameters. Another method requires a simultaneous fit of experimental data to one or other constitutive equation in which a parameter or parameters are related to $\sigma_y$ e.g. [467]:

$$\sigma_{12}(t) = \sigma_y + \eta_0 \dot{\gamma}\{\beta + [(1-\beta)/(1+b\dot{\gamma}^m)][1+b\dot{\gamma}^m \exp\{-kt(1+b\dot{\gamma}^m)/b\}]\} \tag{68}$$

where k is the loss-rate constant, $\beta$ represents the relative residual viscous dissipation parameter, and b and m are parameters originating from the structural breakdown and reformation. Note that for $\dot{\gamma} \to \infty$, $\sigma_{12}/\dot{\gamma} \to \eta_0 \beta = \eta_\infty$. The relation (68) is capable of describing: yield, upper and lower Newtonian plateaux, pseudoplasticity, stress growth and overshoot, thixtropicity, hysterisis, etc. There are also direct methods of $\sigma_y$ measurements. Dzuy and Boger [494] proposed using a specially constructed rotational vane viscometer. Yield stresses in compression and elongation have been measured using standard rheological instruments [423, 426].

3.2.2 Structural and time effects. The phenomenon of yield in flow is associated with a three dimensional structure; $\sigma_y$ is the stress required to break it and cause the flow. In this definition the time scale is not

important; if $\sigma_{12} > \sigma_y$ then the system will instantaneously flow, if $\sigma_y < \sigma_{12}$, it will not. However, the time is important in a number of cases [495]. If $\sigma_{12}$ is small, the measuring time must be correspondingly long. When the measurements are carried out only within the "usual" time scale $\sigma_y$ may be only apparent. However, since in processing the time scale is short the use of the apparent $\sigma_y$ for flow modelling is justified. In PAB the apparent yield stress predominates [259, 260, 386, 475, 476, 496].

Measurements of creep and elastic recovery also provide a direct means of detecting $\sigma_y$. The methods require a simultaneous fit of time dependent strain, $\gamma(t)$, at a constant stress, $\sigma_{12}$, to the creep equation:

$$J(t) = \gamma_{12}(t)/\sigma_{12} = J_0 + J_e\,\psi(t) + t/\eta \qquad (69)$$

where $\psi$ (t) depends on the retardation spectrum.

For $\sigma_{12} < \sigma_y$ the parameters, $J_0$, $J_e$, and $\eta$ are independent of $\sigma_{12}$. Alternatively, plotting the recoverable strain vs imposed stress $\sigma_{12}$, allows detection of $\sigma_y$ as the maximum value of stress below which the Hookean behavior is obtained. The method not only allows separation of time and $\sigma_y$ effects but also permits detection of the critical stresses for structure modification [432, 496, 497].

The dynamic (oscillatory) testing of multiphase systems is a particularly valuable tool. Here the G' and G" are recorded as separate functions of t, T,

$\gamma$ and $\omega$. The structural changes can be detected as discontinuous steps, in these functions, e.g. reported for PET/PA-66 blends [482, 498, 499]. The existence of the stress and/or strain structure transitions indicates that the dynamic and large strain shear flow data for PAB result from morphologically different materials with different properties.

When the dynamic measurements are carried out within the linear viscoelastic region, i.e. in the range of rheological conditions where PAB structure does not change, the data can usually be described in terms of the four constants of Eq (44): $\eta_0$, $\tau^*$, $m_1$, and $m_2$. Careful analysis in terms of MW and MWD [384] indicated that out of those four only $\eta_0$ has a simple correlation

$$\eta_0 = KM_\eta^a; \qquad M_\eta = M_z(M_w/M_n)^{1/5} \tag{70}$$

where $M_n$, $M_w$, $M_z$ and $M_\eta$ are MW-averages in number, weight, z and $\eta$, respectively, K and $a \approx 3.5$ are parameters.

Eq (44) can be used to analytically derive the reduced frequency relaxation spectrum:

$$\tilde{H}_G = (2/\pi) r_h^{-m_2} \sin(m_2 \Theta_h) \tag{71}$$

with $$r_h = [1 + 2(\omega\tau^*)^{m_1} \cos(m_1\pi/2) + (\omega\tau^*)^{2m_1}]^{\frac{1}{2}}$$

and $$\theta_h = \text{arc sin } [(\omega\tau^*)^{m_1} r^{-1} \sin (m\pi/2)]$$

The coordinates of the maximum of $\tilde{H}_G$ vs $\omega$ expressed in terms of $\tau^*$, $m_1$ and $m_2$ have direct correlation with MW and MWD: $\omega_{max} \propto 1/\eta_0$ whereas $\tilde{H}_{G,max} \propto M_n/M_w$. Eqs (44) and (71) allow detection of miscibility in the melt [43]. An example of $\tilde{H}_{G,max}$ vs $M_n/M_w$ for miscible and immiscible LLDPE blends is shown in Figure 18.

## 3.4 Large strain flows

3.4.1 The steady state shear flow predominates in polymer processing. Flow through the extruder, dies and mold runners is controlled by the steady state shear behavior of the material. In rheometry the steady state shear viscosity, $\eta$, is measured either in capillary or rotational instruments. As indicated in part 3.1, besides $\eta$ the two other functions: $N_1$ and $N_2 \approx -0.1N_1$, characterize the flow. While in part 3.3 the strains $\gamma = 2$ to 30% were considered here $\gamma = \dot{\gamma}t$ values of thousands of times higher will be discussed. Due to these differences the structures in dynamic and steady state flows are different which leads to differences in rheological responses [482, 500, 501]. The steps or discontinuities in rheological functions (discussed in part 3.3.2) here are more pronounced [482].

The most dramatic example of different shear behavior between capillary and dynamic flow is that reported for the blend of ethylenepropylene-1,4-hexadiene terpolymer, EPDM, with poly(vinylidene-co- hexafluoropropylene), Viton. While Shih [502, 503] reported a six-fold reduction of shear viscosity

for capillary flow upon addition of 2% or more of the other component Kanu and Shaw [504] demonstrated that $\eta^*$ of EPDM and that of EPDM with 5% Viton are very similar. The latter authors postulated accumulation of the second component at the capillary entrance, which periodically fed into the capillary, lubricating the main stream by a sort of roll bearing effect. The difference between $\eta$ and $\eta^*$ was not related to material properties but rather to a flow segregation enhanced by the geometry of the measuring device.

The value of the dynamic testing of multiphase systems has been increasingly appreciated. It has been extensively used in Japan (Kyoto, Osaka), France (Pau) and in Canada (Montreal, Toronto). Numerous reports from these centers were already cited. Here only two additional ones will be mentioned.

Nishi, Watanabe and Kotaka [505] carried out studies on the dynamic behavior of cast PS/polyvinylmethylether, PVME, at temperatures below and above LCST = 95°C as well as polyvinylidenefluoride, $PVF_2$/ polyethylmethacrylate below its LCST = 200°C. For PS/PVME at $T < LCST$, G' vs $\omega$ showed a usual pattern allowing superposition onto a master curve, but not at $T > LCST$. The plots of isochronal G' or G" vs $w_2$ at 80, 100 and 120°C had a similar sigmoidal shape indicating that phase separation had little bearing on the rheological response.

The group in Pau studied the dynamic properties of polycarbonate, PC, blend with PS [506], with tetramethyl polycarbonate, TMPC, and with both PS and TMPC [507]. The Cole-Cole plot (Fig. 19) for PC (system 1) was a perfect

semicircle, indicating a simple liquid structure. Upon addition of 35 wt% of PS (immiscible system 3) the $\eta''$ vs $\eta'$ dependence can be decomposed into three parts representing PC (the high frequency, low-$\eta'$ data), PS (mid-range) and interphase. In the latter case yield behavior is suspected. The three-component system 2 containing 72% PC, 24% TMPC and 4% PS is significantly simpler. Due to partial miscibility of PC/TMPC blend, again there are two phases but, by contrast with system 3, there is no evidence of yield at low frequencies. From Fig. 19 two relaxation times were defined; both followed Arrhenius dependence with the activation energy of the second about 2.5 times as high as that of the first.

Blend elasticity. Four measures of melt elasticity are commonly used: in steady state shearing $N_1$, in dynamic tests G', and the two indirect and controversial ones, namely entrance-exit pressure drop (Bagley correction), $P_e$, and the extrudate swell, B. In homogeneous melts the four measures are in qualitative agreement. More complex behavior is expected for blends. If the blend can be regarded as an emulsion, in the absence of interlayer slip the PDB behavior for B is to be expected. In systems with $\lambda \approx 1$, the deformation-and-recovery of the dispersed phase provides a potent mechanism for energy storage leading to an elastic response. On the other hand, in systems with $\lambda \gg 1$, where the dispersed phase is difficult to deform, B should be as small as that for suspensions.

The direct measurements of $N_1$ [271, 508-511] indicate a parallel dependence on $\phi$ for both $\eta$ and $N_1$ even when these had a sigmoidal form. In dynamic testing isochronal G' primarily show PDB behavior [474, 512, 513]

although NDB, parallel to $\eta$, was also reported [514].

In the steady state shear flow of a two phase system it is more appropriate to consider the rheological functions in terms of stress than rate [368]. Using a similar argument for the dynamic functions, G' at constant G" should be examined. To illustrate the point in Fig. 20 the isochronal G' is plotted vs weight fraction of the second component for linear low density polyethylene, LLDPE, blends with another LLDPE or with low density polyethylene, LDPE, whereas in Fig. 21 the same data are plotted at G" = const rather than at $\omega$ = const. While in Fig. 20 strong PDB is observed, in Fig. 21 the data show either additivity or NDB; a behavior similar to that of $\eta$ vs $w_2$ [43].

Another method of estimating the elasticity contribution is via the Bagley entrance-exit pressure drop correction, $P_e$. The plot of $P_e$ vs $\sigma_{12}$ for single phase systems is independent of capillary diameter, temperature and molecular weight, but sensitive to changes in flow profile [515]. Furthermore, for a series of polymers with an increasing degree of branching $P_e$ (at $\sigma_{12}$ = const) increases as expected from the network model. The plot was found to be quite useful for interpretation of the stress, temperature and composition-dependent morphological changes in immiscible polymer blends [500, 501]. At low $\phi \lesssim 0.1$ $P_e$ was found to be independent of T and at constant shear stress it increased with loading. At higher concentrations $P_e$ behaved in a complex manner, dependent on $\phi$, T and $\sigma_{12}$.

The extrudate swell, has been used to calculate the recoverable shear

strain, $\gamma_R$, for single phase materials [516, 517]. Introduction of the interface negates the basic theoretical assumptions on which the calculation of $\gamma_R$ was based. In addition, presence of the yield stress prevents B from reaching its equilibrium value required to calculate $\gamma_R$. Nevertheless, B is used as a qualitative measure of blends elasticity [476]. Extrudate swell for rubber compounds was recently reviewed by Leblanc [518]. In several PAB's, B was observed to pass through a maximum at $w_1$ = 50% [473, 477, 519-524]. The presence of a deformable phase leads to enhancement of B. Similar information was obtained from measurements of strain recovery, $\gamma_r$, for PS/PMMA blends [271]. A maximum of $\gamma_r$ was reported at $w_{PMMA}$ = 0.58, coinciding with the longest recovery time. The plot of $\gamma_r$ vs $w_2$ indicated two steps at $w_2$ = 0.27 and 0.78, interpreted by the authors as evidence of phase inversions.

3.4.2 Uniaxial extensional flow behavior of PAB. There are only a few publications on uniaxial deformation of PAB. The specimens for these tests have to be molded and relaxed, both operations requiring the blend to be kept molten for a relatively long time. During this period only well-stabilized blends will not coarsen.

It is convenient to distinguish two contributions to the tensile stress growth function, $\eta_E^+$, one due to linear viscoelastic response, $\eta_{EL}^+$, and the other originating in the structural change of the specimen during deformation, $\eta_{ES}^+$ . The first can be calculated from any linear viscoelastic response, e.g. in shear [43, 385]:

$$\eta_{EL}^{+}(t) = 3\eta_L^{+}(t) = 3\eta_0 \int_{-\infty}^{\infty} \tilde{H}_G \, [1-\exp\{\omega t\}]\, d\ln\omega \qquad (72)$$

where $\tilde{H}_G$ is given by Eq (71). The second component, $\eta_{ES}^{+}$, depends on the intermolecular interactions or entanglements and its value depends on both the total strain, $\varepsilon = \dot{\varepsilon} t$, and either strain rate $\dot{\varepsilon}$ or straining time, t. Due to the industrial importance of strain hardening, SH, a large body of literature focuses on optimization of PAE composition to maximize SH of polyethylenes. The need for better, easier to process film resins, and also for a relative stability of polyolefin blend morphology provides strong motivation. The film blowing involves two operations: extrusion and blowing; most frequently the latter limits productivity. For the low density resins, LDPE, the strain hardening provides a self-healing mechanism. For higher density polyethylenes, HDPE and LLDPE, strain hardening is small. As a result most of these resins are blended with LDPE, rubbers, copolymers or with another type of LLDPE resin. Examples of uniaxial extensional behavior of LLDPE-I/LLDPE-II [515] are show in Fig. 22. SH was also found to be an important resin characteristic in wire coating [525]. La Mantia et al. [526] calculated $\eta_E$ for HDPE/LDPE blends from entrance/exit pressure drop in capillary flow. Min [509] reported $\eta_E$ vs $w_2$ dependence for blends of HDPE with PS, polyamide-6, PA-6 and polycarbonate, PC.

The rheological behavior under extensional, dynamic and steady state shear flow of LLDPE/PP blends were studied by Dumoulin et al. [500]. In spite of immiscibility the blends showed additivity of properties with good superposition of the stress growth functions in shear and elongation. In the

earlier work blends of medium density linear PE, MDPE, with $w_2 \leqslant 0.06$ of ultrahigh molecular weight polyethylene, UHMWPE, were studies in shear and extension. Due to partial dissolution of UHMWPE the blends had the character of a miscible blend with compatible filler particles; $R_T^0 = 1$ and strain hardening were reported [527].

It has been shown [512, 528] that the stress growth function in uniaxial extension provides three important pieces of information on the polymer: the initial slope:

$$S_i = \lim_{t \to 0} [d \ln \eta_E^+ / d \ln t] \tag{73}$$

correlate with polydispersity index $M_w/M_n$. The plateau or equilibrium value provides information on $M_w$ and the stress hardening part, $\eta_{ES}^+$, on entanglement, i.e. branching, association, etc. Since $S_i$ is related to polydispersity (which can be computed for miscible blends,) then it can also be used to test for miscibility [385].

In "antagonistically" immiscible blends of PA-6 in LLDPE a sharp decrease of the maximum strain at break, $\varepsilon_b$, in the investigated range of $w_{PA} \leqslant 0.35$ was observed. In some blends the presence of co-continuous structure around 50:50 composition allows $\varepsilon_b$ to increase to an average value, with negative deviations on both sides [509].

The convergent flow at the die entrance provides a powerful means of

droplets deformation, leading to modification of properties. These effects have been reported for PE with PS, PC, and PA-6 [509, 529, 530], for HDPE with PA-6 [500, 501], or blends containing polymeric liquid crystals, LCP, [531, 532].

### 3.5 Flow-imposed Morphology

The morphology is a science of form and structure, some aspects of which have been discussed in parts 2.3 (NG and SD form), 2.6 (forms imposed by thermodynamics) and 3.2 (structures in filled systems). Now the effects of flow-imposed deformation will be outlined.

By contrast with the deformation during processing (see part 4.1) here effects of a simple deformational field, shear or extensional, will be considered. Most of the theoretical works on flow-imposed morphology assume that: (i) the system consists of dispersed, non-interacting droplets, (ii) the flow is at steady state, (iii) the stress field is uniform, (iv) the time effects on rheological and thermodynamic parameters can be neglected, and (v) the deformations are free from interference by other factors, viz. phase homogenization or ripening, stress-induced crystallization, etc.

There is a multitude of types of flow-induced morphological changes of which flow encapsulation, fiber or platelet formation, shear-induced coalescence, interlayer slip and shear-controlled SD or NG are well documented [368, 375, 472, 475, 476, 500, 501, 509, 529, 530, 533-535].

In Newtonian liquids [536] to achieve maximum dispersion at minimum

expended energy in a steady-state shear flow, $\eta$ of the two liquids should be the same, i.e. in Eq. (60) symbolism $\lambda_0 \approx 1$, where the subscript "$_0$" indicates the Newtonian region. In PAB the above observation has been extended to the non-Newtonian region [537]: $\lambda \to 1$; $\lambda_N \to 1$ in the full range of $\dot{\gamma}$. Since the basic premise of this rule is the existence of the dispersed phase, from Eq. (32) the condition: $\phi_1 \ll 1/2$, should be added.

For increasing values of $\lambda > 1$ it is getting more difficult to disperse liquid 1 in liquid 2. At $\lambda \approx 4$ the energy required to break the droplet becomes so large that the process stops [536]; i.e. at $\lambda_0 \gtrsim 4$ the droplets do not break by shearing, their size being determined by the geometry of the equipment and mechanical slicing. In agreement with this, Berger et al. [538] reported that shearing PAB above $\lambda = 4$ did not reduce droplet size.

For Newtonian liquids, the breaking under shear stress occurs in three stages [430, 539]: 1° deformation of droplets into strands, 2° strand breaking, and 3° reformation of droplets from strand fragments. Defining:

$$\kappa \equiv \sigma_{12} d/\nu \tag{74}$$

(where d is the average droplet diameter), the droplet deformability can be expressed as:

$$D \equiv (d_1-d_2)/(d_1+d_2) = \kappa(19\lambda/16+1)/2(\lambda+1) \tag{75}$$

where $d_1$ and $d_2$ are major and minor axes of the deformed drop. For $D \gtrsim 1/2$ or

for $d_1 \geqslant 3d_2$ the droplet breaks.

For non-Newtonian systems, in the absence of the theoretical analysis, Eqs (74) and (75) should be used only as a guide. Three factors must be considered: (i) the maximum strain at break, $\varepsilon_b$, can be quite large (for LDPE $\varepsilon_b \geqslant 7$, i.e. $d_1 \geqslant 1097d_2$ [539]) (ii) the interfacial tension coefficients in PAB are usually quite small, and (iii) the relaxation times in viscoelastic liquids are long. Due to these factors formation of long fibers under shear (or extensional) stress in PAB is common and relative stability of the flow imposed nonequilibrium structures is quite high.

Krasnikova et al. [540-542] reported that for PE/PS blends at $\phi$ = const in capillary as well as in rotational shear field (cone-and-plate), droplets were formed at shear stress $\sigma_{12} < \sigma_{12,c}$, where:

$$\sigma_{12,c} = a\lambda^b \tag{76}$$

where a and b are constants dependent on $\phi$ and type of blend, and the subscript c indicates a critical value. For PS/PE containing 1, 10 or 30 wt% of PE at $\sigma_{12} \geqslant \sigma_{12,c}$ up to the melt fracture region, formation of fibers was reported (see Fig. 23).

The parameter $\kappa$, which combines the rheological ($\sigma_{12}$) and thermodynamic ($\nu$) functions, allows estimation of the relative ease of dispersing; the larger the $\kappa$ is, the easier it is to disperse [543]. However, $\nu$ is not a

parameter, but a function of time and stress. To determine the equilibrium value of: $\nu = \nu_0$, for commercial polymer blends may require $t > 12$ hrs at the processing temperature [544]. The effect of stress was considered by van Oene [545]:

$$\nu = \nu_0 + (d/12)(N_{1,1}-N_{1,2}) \qquad (77)$$

In the relation, $N_{1,i}$ is $N_1$ of liquid $i = 1$ or 2. The relation has three interesting features: (i) for $N_{1,1} > N_{1,2}$ the interfacial tension increases with shear stress, i.e. droplets are becoming more difficult to break; (ii) for $N_{1,1} < N_{1,2}$ there is a reduction of the interfacial tension and enhancement for generation of fine dispersion at high shear stress; (iii) as $\nu \geqslant 0$ a conversion from droplet to continuous morphology is predicted. The above features lead to complementarity of polymer blend pairs: if, at low content of polymer A in B, a droplet dispersion is observed, at low content of B in A a continuous (fibers or lamellas) morphology is to be expected. Use of Eqs (73), (74) or (76) is difficult due to lack of simple and rapid methods for $\nu$-determination. In commercial polymers, due to the presence of additives (lubricants, processing aids, stabilizers, antioxydants, etc.), the use of a universal value does not make much sense.

Measurements of high stress shear viscosity as well as most of processing involves die flow. The flow through a die is a shear flow with the stress varying linearly from its maximum value on the die wall to zero at the die center (or the limit of plug flow core). However, upstream and downstream

from the die, there are strong extensional fields, respectively convergent and divergent. Cogswell derived the following correlation between extensional viscosity at the entrance to the die and the shear viscosity at the wall [546]:

$$\eta_E/\eta = 2\tan^{-2}\alpha \qquad (78)$$

where $\alpha$ is the half-angle of free convergence given by the ratio of the respective deformation rates:

$$\alpha = \text{arc tan } (2\dot{\varepsilon}/\dot{\gamma}) \qquad (79)$$

i.e. the energy dissipated in shear $\eta\dot{\gamma}^2 = 2\eta_E\dot{\varepsilon}^2$. Recently [547] $\alpha = 20.6 + 1.6°$ was computed for HDPE.

It has been reported [500, 501] that blends of HDPE/PA-6 containing up to 30 wt% of PA-6 and extruded in a capillary viscometer at 150, 200 and 250°C show fibrillation of the PA-6 phase at all temperatures, below and above the melting point of this polymer, $T_m$ = 219°C. The fibrillation was found to be associated with a shear-induced coalescence. The following three other flow-induced morphological changes were reported: (i) A shear-induced segregation of polymer domains, related to encapsulation in flow. A high viscosity ingredient was found to be concentrated in the center of the extruded rod. (ii) Dynamic dispersion/coalescence. For low concentration of disperse phases, it was observed that the average diameter of droplets decreased with $\sigma_{12}$ from its value in pre-blend. (iii) The shear-induced

interlayer slip created a tree-ring structure in the extruded strands readily observed for samples containing 30 wt% of PA-6 in HDPE matrix at $T > T_m$.

There is a reciprocal relation between morphology and flow behavior. Plochocki [537, 548-550] defined the "particular rheological composition", PRC. At PRC $\eta = \eta(\phi)$ function reaches a local maximum or minimum, postulated to be related to a change of morphology. The author also demonstrated that reduction of $\eta$ in immiscible polymer blends is associated with increase of specific volume, most likely due to voiding at the interface.

Bye and Miles [551] measured capillary flow of PS/PMMA and PET/PA-66, blends. For the first system the fluidity additivity Equation (63) with $\beta_1 = 1$ and $w_i$ replaced by $\phi_i$ worked very well. For the second system "as expected for these reactive polymers" the rheological responses were found to depend on history.

Tsebrenko et al. [552] reported that fibrillation of polyoxymethylene, POM in a copolyamide, CPA, matrix resulted in flow through a capillary. As for PA-6 in HDPE matrix [500], here also the droplet undergoes coalescence and stretching in the entrance zone. Very fine fibrils with diameter of about 20μm and length 3200μm were obtained during extrusion at 177°C, i.e. 6°C above POM melting point. In the latter publication [476] the authors reported PDB behavior of $\eta$ and the extrudate swell, B.

## 4. THE MORPHOLOGY OF IMMISCIBLE POLYMER BLENDS DURING PROCESSING

In the previous parts of this chapter some discussion of the morphology with respect to thermodynamics and rheology have already been considered. In this section the objective is to examine the factors controlling the morphology of immiscible blend systems under conditions resembling typical processing environments. Some information concerning droplet break-up in well-defined flow fields will also be presented.

### 4.1 Introduction

The utilization of polymer blends in commerce is growing at a rate of ~10%/year [553]. Blends with engineering resins are growing at ~17%/year [553]. The most important class of blends from the commercial viewpoint are the so-called immiscible blends where the presence of a distinct minor phase (usually in the order of micron size) may be observed [554-558, 129]. The minor phase in an immiscible polymer blend is deformable as opposed to composite materials which contain a rigid minor phase. A wide range of sizes and shapes can thus be obtained for this dispersed phase during processing. Generally, the sizes range from about 0.1μm to 20μm and spherical, ellipsoidal, cylindrical, and ribbon-like morphologies can be prepared. Control of the morphology of immiscible blends during processing is of critical importance but, as yet, remains poorly understood.

The melt rheology of a system is sensitive to morphology [559, 560]. Han et al. [559] in studying PS/PP blends found that even moderately different modes of dispersion and particle size can give rise to pronounced

differences in the apparent rheological properties in the molten state. The size and size distribution of the minor phase has a profound influence on the mechanical properties, especially impact strength.

Impact energy may be dissipated by two main mechanisms [13]. At low loading rates, Type I polymers (e.g. polymethylmethacrylate, polystyrene) exhibit brittle fracture and dissipate energy through crazing. Type II polymers (e.g. polypropylene, nylon, polycarbonate) undergo ductile fracture and shear yielding. Rubber toughening for the former occurs through increased matrix crazing while for Type II the addition of rubber allows for increased matrix yielding. For Type I there exists an optimum particle size of the rubber particle for maximum toughness. For Type II a sharp tough to brittle transition can occur at a critical particle size. For example, in 15% rubber/polyamide blends a fourfold drop in the notched Izod impact strength was observed in increasing the number average particle size from 0.7μm to 0.8μm [561] (see Figure 24). At 25% by weight of a rubber/polyamide blend, a fourfold drop was similarly observed from 1.5μm to 2μm. In the same study it was indicated that it is predominantly a critical surface to surface interparticle distance which determines toughness (see Figure 25). Asar et al. [562] observed in EPDM/PP (ethylene propylene diene terpolymers/polypropylene), blends that local variations in EPDM concentration and domain sizes can result in a twofold difference in the total energy absorbed during impact.

The shape of the minor phase is also of critical importance. Deformation of the minor phase in the direction of extrusion can significantly improve

the elongation at break in the machine direction [563], even in the absence of chemical compatibility. Another novel example of the importance of shape in immiscible blends is illustrated in DuPont's Selar technology [564, 565]. Selar consists of Nylon/PO/Surlyn (polyamide/polyolefin /ionomer comptabilizer) where the minor phase in the form of platelets can result in a significant improvement in barrier properties with respect to oxygen and hydrocarbons (see Figure 26). Some recent work on barrier applications has also considered a polyester matrix [566, 567].

## 4.2 Determination of PAB Morphology by Microscopic Techniques (LM and EM)

One of the main tasks in the microscopic observation of immiscible polymer blends is to achieve good contrast between the phases. This is critical especially if image analysis techniques are to be used to yield quantitative information.

Several microscopic techniques exist to characterize polymer blends [568-570]. Light microscopy in particular may be used when the phase size is larger than 0.5μm. Several methods have been used to improve contrast. If one phase is crystalline and the other amorphous, birefringence effects may be explored [571]. However, for quantitative analysis this technique often yields poor resolution and may be inadequate for good quality particle size analysis. Others have found that the contrast between phases can be improved by raising the temperature of the sample near the melting point of one of the components on a hot-stage. The use of vapours which are specific for the minor phase is one of the most often used methods to improve the contrast [572]. The use of $OsO_4$ to stain elastomeric materials

is one of the more classic examples of this technique. Exposure of a microtomed sample to volatile solvents (e.g. toluene for polystyrene) which specifically dissolve the minor phase can also be used to very effectively improve the contrast [573, 574]. This technique works especially well when the dispersed phase is amorphous. Resolution can also be significantly improved by immersing the sample in oil prior to placing it between the slide and cover glass. This serves to minimize the reflection of light at the surface due to waves in the sample. The use of high contrast film is also adviseable. A short, mild heat treatment (below the melting point of either component) can help to eliminate residual stresses sometimes induced during microtoming without any significant effect on the size and shape of the minor phase).

Electron microscopy is the favoured technique when the particle size is in the sub-micron range. Transmission electron microscopy, TEM, has been used by many authors [575, 576]. It requires, careful sample preparation and specialized equipment; sections less than 1000Å are required. Contrast can be improved through the use of vapours specific for the minor phase as used in light microscopy. Some authors [576] have also found that partial irradiation of the sample can lead to a better resolution.

The scanning electron microscope, SEM, can also be used to examine a dispersed phase of less than 0.5μm. The simplest method of sample preparation is to fracture it under liquid nitrogen. If the adhesion between the two phases is poor, the sample will preferentially fracture at the interface. However, if excellent adhesion exists between the two

phases the components are indistinguishable since fracture will not have necessarily occured at the interface. One weakness of this procedure is that the fracture takes place across several planes and has a tendency to follow the weakest points in the sample. In some cases, therefore the fractured surface may not be representative of the sample as a whole. The latter limitation may be minimized by using thin samples and a pre-notch.

The use of SEM on etched samples is another excellent method of achieving good contrast [573, 577]. The sample is microtomed to an ultra-plane face usually using glass or diamond knives. One important criterion is that the microtoming be carried out at a temperature below the glass transition temperature of the matrix. If this condition is not met, significant ploughing of the dispersed phase through the matrix may occur rendering subsequent image analysis difficult at best and impossible at worst (see Figure 27). After microtoming, the sample is etched in a solvent specific for the minor phase and then observed in the SEM. If the microtoming is properly carried out this procedure can result in excellent contrast between phases even when a high degree of adhesion exists between the components. This technique is excellent especially when the inclusions are of a spherical nature. If more complex morphologies such as ribbons, lamella and fibres are present, transverse and longitudinal sections should be examined. Resolution on the SEM can be further improved by using low voltage (~5-10 kV).

Hobbs & Watkins (578) have reported that good image contrast can be produced by studying the inherent differences in secondary and

backscattered electron emission from the various components of the blend. This method requires the presence of heavy atoms such as bromine in the dispersed phase.

## 4.3 Droplet Breakup in Well-Defined Flow Fields

Einstein [579] developed the expression for the viscosity of dilute hard spheres in suspension. This theory was later extended by Simha [417] to the whole range of concentrations; viz. Eq (51). Rutherford, Taylor and Oldroyd [446] considered the case of the spheres being liquid. In studying Newtonian liquids suspended in another Newtonian liquid, Taylor [580-582] observed that when the radius of the drop was great enough or when the rate of distortion was high, the drops break up. He derived Eq (75) from which one can calculate the size of the largest drop which exists in a fluid undergoing distortion at any rate.

Two basic types of flow were studied by Taylor: uniform shear using a parallel band apparatus and hyperbolic using a four roller apparatus. The basic principle of droplet deformation is that as soon as the disruptive stress due to the viscous drag of the medium is able to overcome the cohesive effect of surface tension, the drop bursts. At high viscosity ratio ($\lambda$ = 20) it was found that the drop still burst in the hyperbolic flow field whereas in uniform shear flow the drop would not burst even at the highest possible speeds. Karam and Bellinger [583] and Tavgac [536] have studied the breakup of Newtonian droplets in a Newtonian matrix over a wide range of viscosity ratios in uniform shear flow. Their results describe a U-type dependence of droplet breakup with viscosity ratio which

indicates that there is an upper and lower limit of viscosity ratio beyond which no breakup occurs (see Figure 28). Karam and Bellinger report that in uniform shearing flow droplet breakup would occur within $0.005 \lesssim \lambda \lesssim 3.0$. Tavgac reported the range as $0.0033 \lesssim \lambda \lesssim 3.7$. At high viscosity ratios the viscous forces which disrupt the drop can not overcome the interfacial forces which keep it together, whereas at very low viscosity ratios the drop was highly deformed, but did not break. An extensional flow field is found to be much more effective for droplet breakup and the limiting viscosity ratio range is much greater than that for uniform shearing flow (see Figure 29) [368, 584].

More recently Grace [585] studied the $\kappa$-parameter at burst versus the viscosity ratio, $\lambda$, over a very wide range, in both shear and hyperbolic flow.

Equations 74 and 75 indicate that the viscosity ratio, the shear stress, the droplet diameter and the interfacial tension are critical variables to consider in controlling particle deformation and breakup in Newtonian fluids.

The dispersed particles may deform and burst in different manners. Mason and Rumscheidt [586], also studying Newtonian fluids, observed different modes of deformation and burst for a spherical drop in hyperbolic and in shear flow (see Figure 30). In shear flow no burst was observed at $\lambda = 6.0$. At $\lambda = 0.7$ the drops were extended into long cylindrical threads which then broke up into a large number of fine droplets. For $\lambda = 1$ the

drop suddenly started to extend into a cylinder which then formed a neck in the middle. The neck thinned until two identical daughter drops and three satellite drops were created. At low viscosity ratio ($\lambda = 2\times10^{-4}$) the drop assumed a sigmoidal shape and fragments of liquid were released from the ends (tip streaming).

In a four-roller apparatus (hyperbolic flow), these same authors found that two modes of deformation and burst were observed. When $\lambda > 0.2$ the drop was pulled out into a thread which then disintegrated into fine droplets by capillary effect. At $\lambda < 0.2$ the ends of the particle drew out into sharp points from which fragments of disperse phase were released by a tip streaming mechanism. Some recent work by Elmendorp has considered capillary instabilities in viscoelastic systems [587-589].

## 4.4 The Influence of Material Properties on Particle Breakup During Processing

Several basic parameters are important to consider in controlling particle deformation of the dispersed phase during processing of polymer blends. They are: viscosity and elasticity ratios, interfacial tension, composition, deformational stress and time of deformation (Deborah number). Much work is required in order to develop a complete understanding. Some relevant articles in this area will be summarized.

4.4.1 Viscosity ratio, $\lambda$. The viscosity ratio has been shown to be one of the most critical variables in controlling blend morphology. Generally high viscosity ratio results in coarse morphology while matching the

viscosities ($\lambda \approx 1$) results in a fine morphology. Avgeropolous et al. [575] have shown by TEM that for a variety of compositions and torque ratios in EPDM/BR blend (ethylene-propylene-diene terpolymer/polybutadiene) the smallest domains are obtained when the mixing viscosities of the components are about equal. They found that the particle size increased with the ratio of mixing viscosities of the components (calculated as torque ratio). The co-continuous phase morphology was also found to relate to the torque ratio and composition. The least viscous component was observed to form the continuous phase over a larger composition range than the more viscous one. At equal mixing viscosities, the co-continuous phase was observed at 50:50 composition. By carefully controlling both the composition and torque ratio the region of the dual-phase continuity of EPDM and BR could be manipulatled from a composition of 0.25BR to 0.75BR (see Figure 31). Careful control of the viscosity ratio through processing parameters such as temperature and shear rate could therefore result in either EPDM or BR forming the dispersed phase.

Wu [590] used image analysis techniques and scanning electron microscopy to characterize the morphology of polyamide/rubber systems during twin-screw extrusion. Since the rubber is much more elastic than the polyamide, this blend system may be considered to represent a viscoelastic drop in a Newtonian matrix case. He showed for this system that viscoelastic drops can breakup during twin-screw extrusion even when $\lambda > 4$. However, due to the complex flow fields, it is impossible to attribute this to either the viscoelastic nature of the dispersed phase or the presence of an extensional flow field. Wu suggested that as the viscosity ratio increases

above unity or decreases below unity the dispersed particles become larger. He also found that the decrease in the dimensions of the minor phase of a chemically modified rubber system compared to the unmodified case were significant and closely related to the decrease in interfacial tension. Furthermore, Wu reported that all the data points for phase size at several viscosity ratios for various sytems gave a single master curve when $\kappa$ was plotted versus the viscosity ratio, $\lambda$; $\kappa$ had the lowest value at $\lambda = 1$. The portion of the curve for $\lambda > 1$ followed a linear dependance.

Karger-Kocsis, Kallo and Kulzenev [577] found for polypropylene/ethylene polypropylene diene terpolymer that there was a linear relationship between the number average diameter of the minor phase (EPDM) and the viscosity ratio. The particle size increased with increasing viscosity ratio. They found that fine dispersions could be achieved if the ethylene content and the $M_n$ of the EPDM impact modifier is low and the viscosity ratio value is near to unity.

Favis and Chalifoux [573] have examined the size of the minor phase of PC/PP blends as a function of $\lambda$. Their samples were mixed in the Brabender mixing chamber, analyzed on the light and scanning electron microscope and then subjected to image analysis. Significant particle deformation was found to occur even at $\lambda = 17.3$. The viscosity ratio was found to have a marked effect on the morphology of the dispersed phase with the phase size increasing by a factor of 3-4 times from $\lambda = 4.5$ to $\lambda = 17.3$ (see Figure 32). Reduction in the size of the minor phase was achieved below $\lambda = 1$ with the minimum particle size occuring at $\lambda \approx 0.15$. This minimum was

found to correspond relatively well to the minimum for Newtonian systems in shear flow. The authors reported observing the onset of upper and lower limits of $\lambda$ beyond which droplet breakup becomes more difficult.

The viscosity ratio can also have an effect on the shape of the minor phase in certain processes. Tsebrenko et al. [552] have shown that in mixtures of polyoxymethylene (POM) with a copolyamide (CPA), the formation of the minor phase into thin fibers takes place at the entry zone in capillary extrusion. The fibre formation is considered to be a result of the stretching and coalescence of individual particles. The onset of stretching and coalescence was observed to occur at a characteristic distance from the capillary entrance. In a later study, Tsebrenko et al. [591] showed that in blends of POM with a copolymer of ethylene and vinyl acetate (CEVAC) POM fibers can be formed in CEVAC only at $\lambda \approx 1$. An increase or decrease in the viscosity of molten POM disrupts fiber formation and results in morphologies resembling films or imperfect fibers. The latter were generally fibers of higher diameter and diameter distribution.

4.4.2 Interfacial Modification. Methods of improving the adhesion at the interface has been discussed in section 2.5. In this part the effect of interfacial modification on the size of the minor phase will be considered in particular. Several tendencies have been observed: 1) the addition of a compatibilizer tends to diminish the phase size since the interfacial tension is reduced; 2) the ability to distinguish the phases in SEM observation of fractured surfaces becomes progressively difficult as

the adhesion is increased and 3) concentrating the interfacial agent in the minor phase by using two-step mixing may be beneficial in producing fine morphologies. D'Orazio et al. [592] showed that the addition of ethylene-propylene random copolymers (EPM) to high density polyethylene (HDPE) or isotactic polypropylene (iPP) blends improves the impact strength of compression-molded specimens. The impact strength of the homopolymers was also improved. They suggest that the EPM copolymers may act as interfacial agents. In many blends of HDPE/EPM no dispersed phase was observed as opposed to the case of iPP/EPM blends which suggests a higher affinity of EPM molecules with HDPE than with iPP.

Cimmino et al. [593] carried out the functionalization of EPM by solution grafting of maleic anhydride molecules using radical initiators. They found that the modified rubber underwent chemical reactions during melt blending with polyamide-6, (PA-6), resulting in a EPM-g-PA-6 graft copolymer. The addition of this modified rubber to PA-6 resulted in significantly improved impact resistance due to the very finely dispersed domains strongly adherent to the PA-6 matrix.

In a later work [594] Cimmino et al. the authors studied the effect of the mixing procedure on PA-6/EPM blends stabilized by an EPM functionalized with maleic anhydride (EPM-g-SA). They considered: 1) one-step mixing in which all these components were introduced into the mixer simultaneously and 2) two-step mixing in which the EPM and EPM-g-SA were premixed prior to mixing with PA-6. The blends which were subjected to one-step mixing showed a very coarse morphology and poor impact strength, whereas those

prepared by two-step mixing had a very fine morphology and excellent impact strength.

Barentsen et al. [595, 596] have shown that the strength and impact properties of polystyrene/low density polyethylene blends can be improved by adding a graft copolymer of polystyrene and low density polyethylene. The presence of the graft copolymer diminishes the particle size of the dispersed phase. They observed that the graft copolymer concentrates at the interface as evidenced by hemispherical bumps of copolymer that become visible on the disperse polymer particles as well as in the holes from which the particles were extracted.

Wu [590] found in polyamide/rubber systems that the particle size was directly proportional to the interfacial tension. The interfacial tension for the rubber/PA system used in his study was $9.7\times10^{-3}$ N/m with a number average particle size for the minor phase of 4.2μm measured experimentally. The interfacial tension for a functionalized rubber/PA blend was $0.25 \times 10^{-3}$ N/m with a particle size of 0.08μm.

4.4.3 Elasticity. The role of the elasticity ratio in determining the size and shape of the minor phase in a polymer blend remains one of the least understood domains in this field. One of the more classical studies in this area was carried out by Van Oene [545]. He has shown that in capillary flow, there are two main modes of dispersion: stratification or droplet-fiber formation. These morphologies were shown to be controlled by the particle size, interfacial tension and the differences in the

viscoelastic properties of the two phases. In mixtures of polystyrene (PS) and polymethylmethacrylate (PMMA), PMMA which had the largest second normal stress function was found to form droplets in the PS matrix. Addition of a low molecular weight PMMA in the same system resulted in stratification. Van Oene noted that when the discrete particles were smaller than a micron, the difference in the morphology of complimentary mixtures (stratification vs. droplets), disappeared indicating that the elastic term contributing to the interfacial tension was no longer dominant. He developed Equation (77) which considers an elastic contribution to the interfacial tension. Van Oene [545] showed that the elastic contribution to the interfacial tension can result in the tendency for a phase of high elasticity to encapsulate one of low elasticity forming composite droplets. He indicated that it is generally difficult to deform a highly elastic material.

Flumerfelt [597] has reported that when Newtonian droplets are broken up in an extensional flow field by a viscoelastic matrix, no lower limiting droplet size was observed beyond which particle disrustion was impossible. This result again emphasizes the efficacy of extensional flow in droplet breakup as described earlier.

4.4.4 Composition. Tokita [598] derived an expression for analyzing the particle size of a dispersed phase in polymer blends. The theory is based on the fact that blending involves the continuous breakdown and coalescence of the dispersed particles. The equilibrium particle size is achieved when the rates of breaking down and coalescence are balanced. The rate constant of breaking the drops is:

$$K_1 = \eta\dot{\gamma}^2/(E_{DK} + 3\nu/R) \tag{80}$$

while the rate constant for coalescence was calculated as:

$$K_2 = (4/\pi)\lambda\phi_D\dot{\gamma} \tag{81}$$

At equilibrium when breaking down and coalescence are balanced: $K_1=K_2=0$, the equilibrium particle size, R* may be expressed as:

$$R^* = [12\lambda\nu\phi_d/(\pi\sigma_{12})][1+4\lambda\phi_d E_{DK}/(\pi\sigma_{12})] \tag{82}$$

where: $\sigma_{12}$ ≡ shear stress, R* ≡ radius of particles, $\nu$ ≡ interfacial tension, $E_{DK}$ ≡ bulk breaking energy, $\phi_d$ ≡ volume fraction of the dispersed phase and $\lambda$ ≡ viscosity ratio. Equation (82) predicts that the equilibrium particle size becomes smaller when the stress field becomes larger, the interfacial tension becomes smaller and the volume fraction of the dispersed phase is smaller. These trends are in agreement with the earlier work by Taylor. This particular development is of particular interest because it includes in its analysis a part considering the effect of composition on phase size.

The effect of composition on phase size is significant. For a blend of PC dispersed in PP of $\lambda$ = 2, the phase size ($d_v$, volume average diameter) increased from 1.2μm at 10% to 5.8μm at 40% [599].

If the entire composition range is studied for a given blend a region of phase inversion with dual-phase continuity is observed. Understanding the factors resulting in this dual-phase continuous morphology are important. It is speculated that this type of morphology would be especially favourable in barrier applications, the tortuosity factor would be expected to be at its maximum in a co-continuous type morphology. One of the main problems, however, is producing samples of appropriate mechanical integrity since there is a high tendency towards delamination and poor mechanical properties for these systems.

Jordhamo, Manson and Sperling [272] reported that the region of dual-phase continuity in mechanical blends of polybutadiene and polystyrene obeyed the rheological viscosity/volume fraction equation shown in Equation (32).

When the left side of the equation was $>1$, phase 2 was the continuous phase. When it was $<1$ phase 1 was continuous. The ability of the low viscosity component to form the continous phase over a larger composition region than the more viscous component may be related to its ease of deformability which allow it to form highly extended bodies.

Favis et al. [599] have shown that Equation (32) does not hold for mechanically mixed blends of PC and PP in a batch type mixing chamber. They studied the morphology over the entire composition range for two blend series of different viscosity ratio and observed distinct regions in the phase size/composition diagram related to dual phase continuity. Changing the torque ratio of the systems from 7 to 2 resulted in a shift of ~10-12

% concentration units for the region of dual-phase continuity (see Figure 33). In these systems however, rather than the low viscosity component forming the continuous phase over a larger composition range than the low viscosity component as predicted by Equation (32), the opposite was observed. The authors suggest that the elasticity ratio may be an important factor in these systems.

4.4.5 Shear stress. The effect of shear stress ($\sigma_{12}$) as considered in Taylor's Equation (75) indicates that the phase size and shear stress are in direct dependence. Wu [590] has shown in PA/rubber blends that changing $\sigma_{12}$ resulted in observable differences in the size of the minor phase. By plotting $\kappa$ vs. $\lambda$ and hence taking into consideration the shear stress variable, all his results fell on a single-line master curve.

In other systems the effect of shear stress on phase size has been less clear. Although large differences in the $\sigma_{12}$ clearly resulted in morphological changes [600, 626], some authors [573, 626] have indicated that varying the shear stress by a factor of two to three has little or no effect on the morphology.

Min et al. [600] noted that for PE/PS (polyethylene/polystyrene) the scale of the phase morphology was made much finer by shearing at high shear stresses. The scale of the morphology with PE/PS was shown to be independent of the mixing temperature from 180°C to 240°C and polyethylene molecular weight even though these variations would be expected to influence the viscosity ratio. In studying polyethylene/polystyrene,

polyethylene/polyamide-6 prepared in the same manner with a single screw extruder and a Koch static mixer, these authors found that the finest phase morphology was found with the PE/PS and the coarsest with PE/polyamide-6 and PP/polyamide-6 [601].

## 4.5 The Effect of Processing Parameters in Compounding and Shaping Operations on PAB Morphology

In this part special emphasis is placed on the importance of processing parameters as opposed to the material based parameters discussed in part 4.4. The dependence of morphology on such variables as energy input, residence time, rotor speed, type of mixing device and screw configuration for extrusion processes will be mentioned. The importance of blend morphology in injection molding will also be considered.

### 4.5.1 Compounding Operations

i) Banbury. The Banbury mixer is one of the most often cited pieces of equipment in batch alloying and has been used especially in rubber-based blends [602]. It is a batch mixer with temperature, pressure and shear rate/stress controls consisting of counter-rotating rotors turning at different speeds usually at around 100 RPM. It has also been adapted to continuous processing in the Farrell Continuous Mixer [603]. The degree of mixing is related to the rotor speed and the time of mixing. Several authors reporting on the operation of internal mixers have found a linear dependence of dispersion with the specific energy input [604-606].

Favis and Chalifoux [607] studying 10% polycarbonate (PC) in polypropylene

(PP) blends in the Brabender mixing chamber found that the particle size was reduced most dramatically in the first two minutes of mixing. Only a very little decrease in the dimensions of the minor phase were observed in increasing the time of mixing to twenty minutes. This observation was confirmed at three different viscosity ratios. It was also observed that variation of the rotor speed from 20 to 80 RPM had no effect on the dimensions of the minor phase. This was observed when either PC or PP was the matrix (at constant volume fraction of minor phase).

Schreiber and Olguin [608] have studied certain polyolefin/elastomer blends under standardized conditions in a Bradender mixing chamber and the sizes of the minor phase were determined by Quantimet analysis. The amount of shear heating during the dispersion of the components varied in inverse proportion with the difference in interfacial tensions of the components. They suggest that this function could be used as a qualitative indication of component miscibility. The average droplet size of the dispersed phase was found to decrease with a closer match of the polymer interfacial tensions. In studying the relationship between phase size vs. energy input they found that the bulk of particle size reduction takes place very early in the mixing process. The dependence of phase size versus energy input then levels out very rapidly. The dispersion was optimized when the melt viscosities of the components were similar.

Plochocki and co-authors [609] have found for LDPE and PS that the size of the minor phase decreases in the order: static mixer (a non-moving part mixing device installed between the heating cylinder and the sprue section

to improve the extent of mixing) > batch distributive mixer (e.g. Banbury) > industrial twin screw dispersive/distributive mixer. These conclusions are supported by recent work in our laborabories [610] where identical blends of PC/PP were compared on the brabender mixing chamber and the twin-screw extruder. Similar blends were processed in the one case at 50 RPM, 250°C and five minutes mixing time in the mixing chamber using roller blades and in another case at 300 RPM, 250°C, on the twin screw extruder using a medium shear screw configuration (this type of configuration consists of 4 zones of kneading elements). The particle size was lower by a factor of ~2 times in the latter case.

ii) Twin-Screw Extrusion. The co-rotating and counter-rotating twin screw extruders are high intensity mixing devices consisting of two screws with a kneading section for intensive mixing. This extruder operates under a "starved feeding mode". It is positive displacing, it allows little leakage between the flights and the barrel (hence precise residence times) and it is capable of imparting high shear through the addition of kneading blocks. The entire screw configuration can be built to fit a particular application (larger shear strains may be imposed on the minor phase by using, in addition to right handed kneading blocks, combinations of elements with right-hand staggered or left-hand staggered configurations).

Eise et al. [611] report that homogenization/mixing of polymer blends on the twin-screw extruder are enhanced by high screw speeds, reduced rates of feeding (low degree of fill) and the use of many kneading blocks. A kneading block consists of a number of kneading discs with specific widths

and staggering angles. Kneading discs can be regarded as elements with 90° flight angles which implies that all flow induced by these elements is in the cross-channel or x-direction.

Bartilla et al. [612] have studied the effect of processing variables in 70:30 (by weight) polypropylene/ethylene propylene diene terpolymers (PP-EPDM) blends extruded on a twin-screw machine. These authors found that the presence of built in baffles (left-handed elements located downstream of the kneading blocks of the plastification zone) resulted in considerably more uniform and finer blends of EPDM in PP. The purpose of these baffles was to make sure that the kneading blocks were completely filled with material and to make sure that no unmelted particles would affect the following processes. The presence of left-handed elements results in drag flow in opposition to the actual transport direction. This results in a type of circulatory flow which increases the average residence time. Increasing the screw speed resulted in more uniform EPDM distribution while increasing the material throughput produced a coarsening of the dispersed phase. Different metering zone geometries showed a perceptible, but only minor effect on EPDM distribution. Narrow tapered discs brought about a narrower elastomer particle size distribution whereas the geometry involving a few side-tapered discs produced numerous large EPDM particles. Compared to the melting zone, the differences achieved in the metering zone were slight. A trend was observed however in the sense that narrow kneading discs were more likely to produce a narrow particle size distribution.

iii) Single-Screw Extrusion. The single screw extruder remains a very common tool for blending polymers due to its widespread availability. It is, however, a relatively poor mixing device due especially to its low shear rates and during the course of a typical mixing experiment the sample in a single screw extruder may experience a wide range of conditions. For example, some of the material which passes between the flights and the barrel can experience high rates of shear while material passing along the channel will be subjected to lower rates of shear. Also, leakage between the flight and the barrel can result in a wide residence time distribution. The improvement of blending on the single screw extruder can be achieved through the use of barrier screws. Barrier screws are fitted with many pins perpendicular to the screw axis which serve to separate the flow and enhance distributive mixing. Without this type of screw a significant variation in phase size may be observed across the cross-section of an extruded strand.

Han et al. [613] carried out a study on the effect of mixing and moulding conditions on the morphology and mechanical properties of polystyrene/polypropylene and polystyrene/polyethylene blends. They compared several mixing devices: screw-plunger, screw-plunger/static mixer, and twin-screw/plunger. The term plunger in this study relates to a piston-like device. The static mixer is a non-moving part mixing device installed between the heating cylinder and the sprue section to improve the extent of mixing. Both the screw-plunger/static mixer and twin-screw machine give slightly improved tensile strengths compared to that obtained by the screw-plunger without a static mixer. The percent elongation at

break was fairly insensitive to the screw mixing devices. The use of the static mixer/plunger is as effective as the screw-plunger machine. The twin screw compounding configuration is not much different than that obtained with a static mixer however the differences could be more pronounced if the viscosities of the individual components were significantly different. Han and co-authors found that the blending ratio was of far greater importance than the mixing device in controlling the mode and degree of dispersion in an immiscible blend.

4.5.2 Injection Molding. The morphology of the minor phase in an injection molded specimen can differ significantly throughout the piece [614-615]. Preferential orientation of the polymer phases may be observed near the wall due to the especially high shear rates experienced. Ho and Salovey [615] have observed for PP/EPDM blends that droplets of EPDM yield flattened ribbons elongated in the direction of melt flow in moulded layers within 400μm of the mold surface or skin and isotropic spherical inclusions were found in the core of the sample. Cielo, Favis and Maldague [616] have also observed elongated fibers at the skin and spherical morphology in the core with 10% PC/PP blends, even though the PC was of significantly higher viscosity than the PP. The phenomenon was especially pronounced at high injection speeds.

Previously in this chapter it has been mentioned that when blending immiscible polymers, the blend viscosity may be less than the viscosities of the individual components [617, 618]. It may be possible therefore to use much lower injection pressures for the blends without necessarily

increasing the molding temperature. However, since the mechanism responsible for NDB is interlayer slip, lamination in injection molded specimens may be expected.

Nolley, Barlow and Paul [619] have found that the mechanical properties followed the sequence (single gated injection molding) > (compression molding) > (double gated injection molding). The problem of weld lines is especially serious for immiscible polymer blends. In a 50:50 blend of PP/LDPE the tensile strength was found to decrease with increased molding temperature. In a study of tensile strength versus composition these authors found that single-gated injection molded blends of PP/LDPE displayed almost additive behaviour. With double-gated specimens the blends were much weaker than the additivity line. In every case, failure occured at the weld line.

Mechanical weakness in double-gated or multi-gated injection-molded specimens at the weldline are due to three main problems [620-623]: 1) slow interdiffusion of polymer molecules after recombination of the two streams; 2) frozen in molecular orientation parallel to the interface caused by fountain flow at the melt front; 3) existance of a V-notch in the sample due to the presence of entrapped air or contaminents.

Brittle polymers are particularly susceptible to weld line problems and the presence of a second phase can exaggerate this weakness due to the preferential orientation of the dispersed phase at the weld-line interface. The most common method of minimizing weld line problems is to

process at higher melt temperatures. Relatively few studies have been carried out on weld lines in polymer blend systems, more research is needed in this area to effectively minimize this very serious limitation.

REFERENCES


1. T. HANCOCK, Engl. Pat., No. 11, 147 (1846).
2. R.F. BAUER, Polym. Eng. Sci., 22, 130 (1982).
3. R.B. SEYMOUR, Ed., "History of Polymer Science and Technology", M. Dekker, Inc., New York, (1982); H. MORAWETZ, "Polymers: The Origins and Growth of a Science", J. Wiley & Sons, New York (1985).
4. A.S. HAY, Polym. Eng. Sci., 16, 1 (1976).
5. G.A. ZAKRZEWSKI, Polymer, 17, 348 (1973).
6. P.C. JULIANO in "Panel and General Discussion", L.A. Utracki, Ed., NRCC/IMRI symposium "Polyblends-'84", Boucherville, Que., Canada, 17 April 1984; Polym. Eng. Sci., 24, 1359 (1984).
7. L.A. UTRACKI, "Polymer Blends; Their Preparation Processing and Economic Forecast", DSI-UNDP seminar on Recent Trends in Polymers and Their Composites, New Delhi, India, December 17-21, 1986.
8. H. KESKKULA, Ed., Polymer Modifications of Rubber and Plastics", Appl. Polym. Symp., 7, J. Wiley and Sons, New York (1968).
9. P.F. BRUINS, Ed., "Polyblends and Composites", Appl. Polym. Symp., 15, J. Wiley and Sons, New York (1970).
10. A.J. PLATZER, Ed., "Copolymers, Polyblends and Composites," A.C.S., Adv. Chem. Ser., 142, Washington, D.C. (1975).
11. J.A. MANSON and L.H. SPERLING, "Polymer Blends and Composites," Plenum Press, New York (1976).
12. D. KLEMPNER and K.C. FRISCH, Eds., "Polymer Alloys", Plenum Press, New York (1977); "Polymer Alloys II", Plenum Press, New York (1980).

13. C. BUCKNALL, "Toughened Plastics", Appl. Sci. Publ., London (1977).

14. D.R. PAUL and S. NEWMAN Eds., "Polymer Blends," Academic Press, New York (1978).

15. J.L. COOPER and G.M. ESTES Eds., "Multiphase Polymers," A.C.S. Adv. Chem. Ser., 176, Washington, D.C. (1979).

16. D. KLEMPNER and K.C. FRISCH, Eds., "Polymer Alloys III", Plenum Press, New York (1983).

17. O. OLABISI, L.M. ROBESON, and M.T. SHAW, "Polymer-Polymer Miscibility", Academic Press, New York (1979).

18. K. SOLE, Ed., "Polymer Compatability and Incompatibility", MMI Press, Chur, Switzerland (1982).

19. O. OLABISI, "Polyblends," Kirk-Othmer Encyclopedia of Chemical Technology, J. Wiley and Sons, New York (1982).

20. M.T. SHAW, Ed., "The Plastics ABC's: Polymer Alloys Blends and Composites", S.P.E. NATEC, Miami, FA, Oct. 1982; Polym. Eng. Sci., 23 (11, 12)(1983).

21. C.D. HAN, Ed., "Polymer Blends and Composites in Multiphase Systems," A.C.S., Adv. Chem. Ser., 206, Washington, D.C. (1984).

22. D.R. PAUL and L.H. SPERLING, Eds., "Multicomponent Polymer Materials", A.C.S., Adv. Chem. Ser., 211, Washington, D.C. (1986).

23. L.A. UTRACKI, Ed., NRCC/IMRI Ann. Intl. Symp., "Polyblends-'80" through to "Polyblends-'87", Polym. Eng. Sci., 22(2) (1982); 22(17) (1982); 24(2) (1984); 24(17) (1984); 26(1) (1986); 27(5 and 6) (1987); 28 ( ) (1988)

24. H. TOMPA, "Polymer Solutions", Butterworths Sci. Publ., London (1956).

25. M.L. HUGGINS, J. Chem. Phys., 9, 440 (1941).

26. P.J. FLORY, J. Chem. Phys., 9, 660 (1941).

27. D.D. PATTERSON and A. ROBARD, Macromolecules, 11, 690 (1978).

28. D. McINTYRE, N. ROUNDS and E. CAMPOS-LOPEZ, A.C.S., Polym. Prepr., 10, 531 (1969).

29. R. KONINGSVELD, L.A. KLEINJENS and H.M. SCHOFFALEERS, Pure Appl. Chem., 39, 1 (1974).

30. M.H. ONCLIN, L.A. KLEINJENS, and R. KONINGSVELD, Brit. Polym. J., 12, 221 (1980).

31. R. KONINGSVELD, M.H. ONCLIN and L.A. KLEINTJENS, in "Polymer Compatability and Incompatability", K. Šolc, Ed., MMI Press, New York (1982).

32. R. KONINGSVELD, L.A. KLEINTJENS and M.H. ONCLIN, J. Macromol. Sci., Phys., B18, 363 (1980).

33. M.L. HUGGINS, J. Phys. Chem., 80, 1317 (1976).

34. P.J. FLORY, R.A. ORWOLL and A. VRIJ, J. Amer. Chem Soc., 86, 3515 (1964).

35. B.E. EICHINGER and P.J. FLORY, Trans. Faraday Soc., 64, 2035 (1968).

36. I.C. SANCHEZ and R.H. LACOMBE, J. Phys. Chem., 80, 2352 (1976); J. Polym. Sci., Polym. Lett. Ed., 15, 17 (1977).

37. I.C. SANCHEZ, Ann. Rev. Mater. Sci., 13, 387 (1983).

38. A. EISENBERG and M. HARA, NRCC/IMRI symposium "Polyblends-'84" Boucherville, Que., Canada, 17 April 1984; Polym. Eng. Sci., 24, 1306 (1984).

39. P. SMITH, M. HARA and A. EISENBERG, in "Current Topics in Polymer

Science", R.M. Ottenbrite, L.A Utracki and S. Inoue, Eds., Hanser Verlag, München, FRG (1987).

40. I.G. KAPLAN, "Theory of Molecular Interactions", Elsevier, Amsterdam (1986).

41. F.M. FOWKES, D.O. TISCHLER, J.A. WOLFE, L.A. LANNIGAN, C.M. ADEMU-JOHN and M. HOLLIWELL, J. Polym. Sci., Polym. Chem. Ed., 22, 547 (1984).

42. L.M. ROBESON in ref. 18.

43. L.A. UTRACKI and B. SCHLUND, Polym. Eng. Sci. 28, 000 (1988).

44. D.R. PAUL, "Miscibility in Polymer Blends", presented at Phase Equilibrium in Polymer Blends symposium Univ. Connecticut, Stores, CT, May 1 (1981).

45. D.R. PAUL and J.W. BARLOW, Polymer, 25, 487 (1984).

46. F.E. KARASZ, 68th Conf. Chem. Inst. Canada, Kingston, Ont., Canada, 2-5 June (1985).

47. T. SHIOMI, F.E. KARASZ and W.J. MacKNIGHT, Macromolecules, 19, 2274 (1986).

48. T.K. KWEI and T.T. WANG, Ch. 4 in ref. [14].

49. J.M. LIFSHITZ and V.V. SLYOZOV, J. Phys. Chem. Solids, Lett. Sect., 19, 35 (1961).

50. J.S. LANGER, in "Fluctuations, Instabilities and Phase Transitions", T. Riste, Ed., Plenum Press, New York, 1977; "Kinetics of Metastable States", Lect. Notes Phys., 132, 12 (1980).

51. J.W. CAHN and J.E. HILLIARD, J. Chem. Phys., 28, 258 (1958).

52. H.L. SNYDER, P. MEAKIN and S. REICH, Macromolecules, 16, 757 (1983).

53. H.L. SNYDER and P. MEAKIN, J. Chem. Phys., 79, 5588 (1983).

54. H.L. SNYDER and P. MEAKIN, private communication (1984).

55. I.G. VOIGT-MARTIN, K.H. LEISTER, R. ROSENAU and R. KONINGSVELD, J. Polym. Sci., Part B: Polym. Phys., 24, 723 (1986).

56. R. PETSCHEK and H. METIU, J. Chem. Phys., 79, 3443 (1983).

57. P. MEAKIN, H. METIU, R.G. PETSCHEK and D.J. SCALPINO, J. Chem. Phys., 79, 1948 (1983).

58. H.E. COOK, Acta. Metall., 18, 297 (1970).

59. J.S. LANGER, Physica (Utrecht), 73, 61 (1974).

60. J.S. LANGER, M. BAR-ON and H.D. MILLER, Phys. Rev., A11, 1417 (1975).

61. K. KAWASAKI and T. OHTA, Prog. Theoret. Phys., 59, 362 (1978).

62. T. OHTA and K. KAWASAKI, Phys. Lett., 64A, 404 (1978).

63. E.D. SIGGIA, Phys. Rev., A20, 595 (1979).

64. T. HASHIMOTO, in "Current Topics in Polymer Science", R.M. Ottenbrite, L.A. Utracki and S. Inoue, Eds., Hanser Verlag, München, FRG (1987).

65. L. LEIBLER, Macromolecules, 13, 1602 (1980).

66. I. YA YERUKHIMOVICH, Vysokolmol. Soed., A24, 1942 (1982); ibid. A24, 1950 (1982).

67. P.G. de GENNES, "Scaling Concepts in Polymer Physics", Cornell University Press, Ithaca, New York (1979).

68. P.G. de GENNES, J. Chem. Phys., 55, 572 (1971).

69. J.F. JOANNY, C.R. Acad. Sci. (Paris), 286B, 89 (1978).

70. M.A. MOORE, J. Phys. A, Math. Gen., 10, 305 (1977).

71. I.M. LIFSCHITZ, A. GROSBERG and A. KHOKHLOV, Rev. Mod. Phys., 50, 685 (1978).

72. J.F. JOANNY, PhD thesis (3ème cycle), University of Paris 6, (1978);

J. Phys. A: Math. Gen., 11, L117 (1978).

73. P.G. de GENNES, J. Chem. Phys., 72, 4756 (1980).

74. J.F. JOANNY and F. BROCHARD, J. Physique, 42, 1145 (1981).

75. P. PINCUS, J. Chem. Phys., 75, 1996 (1981).

76. F. BROCHARD and P.G. de GENNES, Physica, 118A, 289 (1983).

77. R. GELLES and C.W. FRANK, Macromolecules, 16, 1448 (1983).

78. C. HERKT-MAETZKY and J. SCHELTEN, Phys. Rev. Lett., 51, 896 (1983).

79. J.H. WENDERHOFF, J. Polym. Sci., Polym. Lett. Ed., 18, 439 (1980).

80. K. KAMIDE and Y. MIYAZAKI, Polym. J., 13, 325 (1981).

81. B. WUNDERLICH, "Macromolecular Physics", Vol. 2: "Crystal Nucleation, Growth and Annealing", (1976); Vol. 3: "Crystal Melting", (1980), Academic Press, New York, N.Y.

82. J.D. HOFFMAN and J.I. LAURITZEN, J. Res. N.B.S., Sec. A, A65, 297 (1961); J.I. LAURITZEN and J.D. HOFFMAN, J. Appl. Phys., 44, 4430 (1973).

83. M.I. ILLIN, YU. V. SHARIKOV, A.A. ZHITINKIN and P.V. CHERNYAVSKII, Theor. Osnovy Khim. Tekhnol., 17, 44 (1983).

84. S. KENIG and M.R. KAMAL, S.P.E. J., 26, 50 (1970).

85. M.R. KAMAL and P.G. LAFLEUR, Paper presented during NRCC/IMRI mini-symposium "Modelling-'83", Montreal, Feb. 9th, 1983; Polym. Eng. Sci., 24, 692 (1984); ibid., 26, 103 (1986).

86. P.G. LAFLEUR and M.R. KAMAL, Polym. Eng. Sci., 26, 92 (1986).

87. T.NISHI and T.T. WANG, Macromolecules, 8, 909 (1975); ibid., 10, 421 (1977).

88. B. RIEDL and R.E. PRUD'HOMME, Paper presented at the 5th NRCC/IMRI

mini-symposium "Polyblends-'84", Boucherville, P.Q., April 17, 1984; Polym. Eng. Sci., 24, 1291 (1984).

89. A.A. REMIZOVA, S.A. KUPTSOV and F.G. GILIMYANOV, Plast. Massy, (4), 12 (1983).

90. S. HORIKIRI and K. KODERA, Polym. J., 4, 213 (1973).

91. O.F. NOEL III and J.E. CARLEY, Polym. Eng. Sci., 24, 488 (1984).

92. B.S. MORRA and R.S. STEIN, Polym. Eng. Sci., 24, 311 (1984).

93. J. PLANS, W.J. MacKNIGHT and F.E. KARASZ, Macromolecules, 17, 1100 (1984).

94. H.W. STARKWEATHER, Jr., J. Appl. Polym. Sci., 25, 139 (1980).

95. D.R. PAUL and J.W. BARLOW, A.C.S., Div. Org. Coat. Plast. Chem. Preprints, 40, 745 (1979).

96. J.M. BARLOW and D.R. PAUL, NRCC/IMRI symposium, "Polyblends-87" Boucherville, Que. Canada, Apr. 28-29, 1987; Polym. Eng. Sci., 28, 000 (1988).

97. J.W. BARLOW and D.R. PAUL, Ann. Rev. Mater. Sci., 11, 299 (1981).

98. J.E. HARRIS, D.R. PAUL and J.W. BARLOW, Polym. Eng. Sci., 23, 676 (1983); A.C.S., Adv. Chem. Ser., 206, 43 (1984).

99. D.R. PAUL and J.W. BARLOW, Proceed. 28th IUPAC Meeting, Amherst, MA, July 12-16, 1982, pg. 684.

100. P.J. FLORY, "Principles of Polymer Chemistry", Cornell University Press, Ithaca, New York (1953).

101. L.A. UTRACKI, J. Appl. Polym. Sci., 6, 399 (1962).

102. R. KONINGSVELD and A.J. STAVERMAN, J. Polym. Sci., Part A-2, 6, 349 (1968).

103. G. ALLEN, G. GEE and J.P. NICHOLSON, Polymer, 2, 8 (1961).

104. R. KONINGSVELD and L.A. KLEINTJENS, J. Polym. Sci., Polym. Symp., 61, 221 (1977).

105. J. KOHLER, G. RIESS and A. BANDERET, Eur. Polym. J., 4, 173 (1968).

106. T. NISHI and T.K. KWEI, Polymer, 16, 285 (1975).

107. D.D. DAVIS and T.K. KWEI, J. Polym. Sci., Polym. Phys. Ed., 18, 2337 (1980).

108. E. ROERDINK and G. CHALLA, Polymer, 19, 173 (1978); ibid., 21, 1161 (1980).

109. G. ten BRINKE, A. ESHUIS, E. ROERDINK and G. CHALLA, Macromolecules, 14, 867 (1981).

110. G. Ten BRINKE, E. ROERDINK and G. CHALLA, in ref. [18].

111. S.H. GOH, D.R. PAUL and J.W. BARLOW, Polym. Eng. Sci., 22, 34 (1982).

112. N. HIROMATSU, S. HASHIDA, M. YASUNIWA and S. HIRAKAWA, Fukuoka Daigaku Rigaku Shuho, 13, 39 (1983).

113. D.J. WALSH and J.G. McKEOWN, Polymer, 21, 1330, 1335 (1980).

114. H. JAGER, E.J. VORENKAMP and G. Challa, Polym. Comm., 24, 290 (1983).

115. H.L. SNYDER, P. MEAKIN and S. REICH, Macromolecules, 16, 757 (1983); J. Chem. Phys., 78, 3334 (1983); A.C.S., Polym. Prepr., 24, 411 (1983).

116. W.-Ch, ZIN, PhD thesis, Univ. Cincinnati (1983).

117. W.-Ch. ZIN and R.-J. ROE, Macromolecules, 17, 183 (1984).

118. R.-J. ROE and W.-Ch. ZIN, Macromolecules, 17, 189 (1984).

119. S.H. GOH, K.S. SIOW, T.T. NGUYEN and A. NAM, Eur. Polym. J., 20, 65 (1984).

120. Ch. SHAO-CHENG, PhD thesis, Univ. Maryland (1981).

121. D.J. WALSH, S. LAINGHE and Ch. ZHIKUAN, Polymer, 22, 1005 (1981).

122. D.J. WALSH, J.S. HIGGINS and Ch. ZHIKUAN, Polymer, 23, 336 (1982).

123. D.J. WALSH, J. S. HIGGINS and S. ROSTAMI, Macromolecules, 16, 388 (1983).

124. D.J. WALSH, J.S. HIGGINS, S. ROSTAMI and K. WEERAPERUMA, Macromolecules, 16, 391 (1983).

125. S. ROSTAMI and D.J. WALSH, Macromolecules, 17, 315 (1984).

126. L.P. McMASTER, Macromolecules, 6, 760 (1973).

127. K.S. SHIH and C.L. BEATTY, A.C.S., Org. Coat. Plastics Chem. Div. Preprints, 45, 65 (1981).

128. R.H. SOMANI and M.T. SHAW, A.C.S., Org. Coat. Plastics Chem., 45, 592 (1981).

129. M.T. SHAW, NRCC/IMRI symposium, "Polyblends-'81", Montreal Que. Canada, April 28, 1981; Polym. Eng. Sci., 22, 115 (1982).

130. R.H. SOMANI and M.T. SHAW, Macromolecules, 14, 886 (1981).

131. R.H. SOMANI and M.T. SHAW, Macromolecules, 14, 1549 (1981).

132. M.T. SHAW and R.H. SOMANI, A.C.S., Adv. Chem. Ser., 206, 33 (1984); Polym. Eng. Sci., 24, 601 (1984).

133. R.H. SOMANI, MSc thesis, Univ. Connecticut, Storrs, CT (1981).

134. M. GORDON, J. GOLDSBROUGH, B.W. READY and K. DERHAM, in "Industrial Polymers", J.H.S. Green and R. Dietz. Eds., Transcripta Books, London (1973).

135. K.W. DERHAM, J. GOLDSBROUGH and M. GORDON, Pure Appl. Chem., 38, 97 (1974).

136. J.W. KENNEDY, M. GORDON and G. ALVAREZ, Polimery (Warsaw), 20, 463

(1975).

137. M. GORDON, L.A. KLEINTJENS, B.W. READY, and J.A. TORKINGTON, Br. Polym. J., 10, 170 (1978).

138. M. GORDON and B.W. READY, U.S. Pat. 4,131,369, Dec. 26, (1978).

139. M. ONCLIN, L.A. KLEINTJENS and R. KONINGSVELD Makromol. Chem. Suppl., 3, 197 (1979).

140. M.H. ONCLIN, PhD thesis, Antwerp (1980).

141. L.A. KLEINTJENS, M.H. ONCLIN and R. KONINGSVELD Symp., Berlin (1980).

142. F.B. KHAMBATA, PhD thesis, Univ. Massachusetts, Amherst (1976).

143. T.P. RUSSELL, PhD thesis, Univ. Massachusetts, Amherst (1979).

144. T.P. RUSSELL and R.S. STEIN, J. Polymer Sci., Polymer Phys., 20, 1593 (1982); ibid., 21, 999 (1983).

145. R.S. STEIN, G. HADZIIOANNOU, M. WAI, J. GILMER, F. HEROLD and B. MORRA, A.C.S., Org. Coat. Plastics Chem. Div. Prepr., 45, 80 (1981).

146. L.H. SPERLING, Polym. Eng. Sci., 24, 1 (1984).

147. A. KELLER, Inst. Phys. Conf. Ser., 64, 317 (1983).

148. R.G. KIRSTE and B.R. LEHNEN, Makromol. Chem., 177, 1137 (1976).

149. W.A. KRUSE, R.G. KIRSTE, J. HAAS, B.J. SCHMITT and D.J. STEIN, Makromol. Chem., 177, 1145 (1976).

150. J. JELENIC, R.G. KIRSTE, B.J. SCHMITT and S. SCHMITT-STRECKER, Makromol. Chem., 180, 2057 (1979).

151. G.D. WIGNALL, H.R. CHILD and F. LI-ARAVENA, Polymer, 21, 131 (1980).

152. R.P. KAMBOUR, R.C. BOPP, A. MACONNACHIE and W.J. MacKNIGHT, Polymer, 21, 133 (1980).

153. B.J. SCHMITT, R.G. KIRSTE, and J. JELENIC, Makromol. Chem., 181, 1655

(1980).

154. B.J. SCHMITT, Angew. Chem., 91, 286 (1979); Angew Chem., Int. Ed. Engl., 18, 273 (1979).

155. J. JELENIC, R.G. KIRSTE, R.C. OBERTHÜR, S. SCHMITT-STRECKER and B.J. SCHMITT, Macromol. Chem., 185, 129 (1984).

156. A. MACONNACHIE, R.P. KAMBOUR and R.C. BOPP, Polymer, 25, 357 (1984).

157. C.W. FRANK, Plastic Comp., pp. 67-74, Jan./Feb. (1981).

158. M.A. WINNIK, NRCC/IMRI symposium "Polyblends-'83", April 12, 1983, Montreal, P.Q. Canada; Polymer Eng. Sci., 24, 87 (1984); L.S. Egan and M.A. WINNIK, ibid. 26, 15 (1986).

159. C.W. FRANK, M.-A. GARSHGARI, P. CHUTIKAMONTHAM and V.J. HAVERLY, Stud. Phys. Theor. Chem., 10, 187 (1980).

160. S.N. SEMERAK and C.W. FRANK, Macromolecules, 14, 443, (1981).

161. A. YA. MENZHERES and E.G. MOISYA, Kompoz. Polim. Mater., 17, 14 (1983).

162. M.-A.D. GASHGARI, PhD thesis, Stanford Univ., CA (1983).

163. S. SEMERAK, PhD thesis, Stanford Univ., CA (1983).

164. S.N. SEMERAK and C.W. FRANK, Macromolecules, 17, 1148 (1984).

165. H. MORAWETZ and F. AMRANI, Macromolecules, 11, 281 (1978).

166. H. MORAWETZ, Pure Appl. Chem., 52, 277 (1980).

167. K. NAITO and T.K. KWEI, J. Polym. Sci., Polym. Chem. Ed., 17, 2935 (1979).

168. K. NAITO and T.K. KWEI, Polym. Eng. Sci., 19, 841 (1979).

169. G. DiPAOLA-BARANYI, Macromolecules, 14, 1457 (1981).

170. G. DiPAOLA-BARANYI and P. DEGRE, Macromolecules, 14, 1456 (1981).

171. G. DiPAOLA-BARANYI, S.J. FLETCHER and P. DEGRE, Macromolecules, 15, 885

(1982).

172. G. DiPAOLA-BARANYI, J. RICHER and W.M. PREST Jr., Can. J. Chem., 63, 223 (1985).

173. Yu. S. LIPATOV, A. Ye. NESTEROV, T.D. IGNATOVA, V.F. SHUMSKII and A.N. GORBATENKO, Vysokomol. Soed., A24, 549 (1982).

174. A.N. GORBATENKO, T.D. IGNATOVA, V.F. SHUMSKII, A. Ye. NESTEROV, Yu. S. LIPATOV, L.S. BOLOTNIKOVA and Yu. N. PANOV, Kompoz. Polim. Mater., 15, 18 (1982).

175. C. ZHIKUAN and D.J. WALSH, Eur. Polym. J., 19, 519 (1983).

176. J.M. ELORZA, M.J. FDZ-BERRIDI, J.J. IRUIN and G.M. GUZMAN, Polym. Eng. Sci., 24, 287 (1984).

177. V. NARASIMHAN, D.R. LLOYD and C.M. BURNS, J. Appl. Polym. Sci., 23, 749 (1979).

178. V. NARASIMHAN, R.Y.M. HUANG and C.M. BURNS, J. Polym. Sci., Phys. Ed., 21, 1993 (1983).

179. V. NARASIMHAN, C.M. BURNS, R.Y.M. HUANG and D.R. LLOYD, A.C.S., Adv. Chem. Ser., 206, 3 (1984).

180. W.W.Y. LAU, C.M. BURNS and R.Y.M. HUANG, J. Appl. Polym. Sci., 29, 1531 (1984).

181. R.F. Boyer, J. Polym. Sci., Part C, 14, 267 (1966).

182. R.W. WARFIELD and B. HARTMANN, Polymer, 21, 31 (1980).

183. D.S. KAPLAN, J. Appl. Polym. Sci., 20, 2615 (1976).

184. H.E. BAIR and P.C. WARREN, J. Macromol. Sci., Phys., B20, 381 (1981).

185. K.C. FRISCH, D. KLEMPNER and H.L. FIRSCH, NRCC/IMRI symposium "Polyblends-'82", Montreal, Que. Canada, April 20, 1982; Polym. Eng.

Sci., 22, 1143 (1982).

186. A.R. SHULTZ and A.L. YOUNG, Macromolecules, 13, 663 (1980).

187. L.A. UTRACKI, Adv. Polym. Technol., 5, 33 (1985).

188. P.R. COUCHMAN, Macromolecules, 11, 1156 (1978).

189. Ch. L. RYAN Jr. PhD thesis, Univ. Massachusetts, Amherst, MA (1979); J.R. FRIED, F.E. KARASZ and W.J. MacKNIGHT, Macromolecules, 11, 150 (1978).

190. R.A. MENDELSON, private communication (1984).

191. E.F. JORDAN, Jr., B. ARTYMYSHYN and G.R. RISER, J. Appl. Polym. Sci., 20, 2757 (1976).

192. R. SIMHA, Macromolecules, 10, 1025 (1977).

193. J.M. RODRIGUEZ - PARADA and V. PERCEC, Macromolecules, 19, 55 (1986).

194. P.S. ALEXANDROVICH, PhD thesis, Univ. Massachusetts, Amherst, MA (1978).

195. V.J. McBRIERTY, D.C. DOUGLASS and P.J. BARHAM, J. Polym. Sci., Polym. Phys. Ed., 18, 1561 (1980).

196. S. KAPLAN and J.J. O'MALLEY, A.C.S., Polym. Prepr., 20(2), 266 (1979), Polymer, 22, 221 (1981).

197. J. SCHAEFER, M.D. SEFCIK, E.O. STEJSKAL and R.A. McKAY, Macromolecules, 14, 188 (1981); A.C.S., Polym. Prepr., 20(2), 747 (1979).

198. E.O. STEJSKAL, J. SCHAEFER, M.D. SEFCIK and R.A. McKAY, Macromolecules, 14, 275 (1981).

199. R. KOSFELD and L. ZUMKLEY, Colloid Polym. Sci., 260, 198 (1982); in ref. [18].

200. V.S. DERINOVSKII, I.N. ZAKIROV, V.M. LANTSOV, V.P. VOLKOV and B.A.

ROZENBERG, Vysokomol. Soed., A24, 2390 (1982).

201. L.W. JELINSKI, J.J. DUMAIS, F.C. SCHILLING and F.A. BOVEY, A.C.S., Symp. Ser., 191, 345 (1982).

202. E. MARTUSCELLI, G. DEMMA, E. ROSSI and A.L. SEGRE, Polym. Comm., 24, 266 (1983).

203. S. NAGARAJAN and Z.H. STACHURSKI, J. Polym. Sci., Polym. Phys. Ed., 20, 989 (1982).

204. T.S. LIN and T.C. WARD, A.C.S., Polym. Prepr., 24(2), 136 (1983).

205. T.C. WARD and T.S. LIN, A.C.S., Adv. Chem. Ser., 206, 59 (1984).

206. D.C. DOUGLASS, A.C.S., Polym. Prepr., 20(2), 251 (1979).

207. W.W. FLEMING, J.R. LYERLA and C.S. YANNONI, A.C.S., Symp. Ser., 247, 83 (1984).

208. R. JANIK and J. PLUCINSKI, Przemysl Chem., 59, 555 (1980).

209. M.B. DJORDJEVIC and R.S. PORTER, A.C.S., Polym. Prepr., 22(2), 323 (1981).

210. M.B. DJORDJEVIC and R.S. PORTER, NRCC/IMRI Symposium "Polyblends-'82", Montreal, Que. Canada, April 20, 1982; Polym. Eng. Sci., 22, 1109 (1982); Polym. Eng. Sci., 23, 650 (1983).

211. A. GARTON, P. COUSIN and R.E. PRUD'HOMME, J. Polym. Sci., Polym. Phys. Ed., 21, 2275 (1983).

212. P. COUSIN and R.E. PRUD'HOMME, A.C.S., Div. Polym. Mat. Sci. Eng., 51, 291 (1984).

213. P. COUSIN, R.E. PRUD'HOMME and A. GARTON in "Current Topics in Polymer Science", R.M. Ottenbrite, L.A. Utracki and S. Inoue, Eds., Hanser Publ., München, FRG (1987).

214. J.L. KOENIG, Adv. Polym. Ser., 54, 87 (1983).

215. W. KLÖPFFER, "Introduction to Polymer Spectroscopy", Springer Publ., Berlin, FRG (1984).

216. M.M. COLEMAN and D.F. VARNELL, J. Polym. Sci., Polym. Phys. Ed., 18, 1402 (1980).

217. D.F VARNELL and M.M. COLEMAN, Polymer, 22, 1324 (1981).

218. D.F. VARNELL, PhD thesis, Pennsylvania State Univ. (1982).

219. M.M. COLEMAN, D.F. VARNELL and J.P. RUNT, Polym. Sci. Techn., 20, 59 (1983).

220. D.F. VARNELL, J.P. RUNT and M.M. COLEMAN, Polymer, 24, 37 (1983).

221. M.M. COLEMAN, E.J. MOSCALA, P.C. PAINTER, D.J. WALSH and S. ROSTAMI, Polymer, 24, 1410 (1983).

222. D.F. VARNELL, E.J. MOSKALA, P.C. PAINTER and M.M. COLEMAN, Polym. Eng. Sci., 23, 658 (1983).

223. R.E. PRUD'HOMME, NRCC/INRI Symposium, "Polyblends-81", Montreal, Que. Canada, April 28, 1981; Polym. Eng. Sci., 22, 1138 (1982).

224. A. GARTON, M. AUBIN and R.E. PRUD'HOMME, J. Polym. Sci., Polym. Lett. Ed., 21, 45 (1983).

225. M. ISKANDAR, C. TRAN, L.M. ROBESON and J.E. McGRATH, Polym. Eng. Sci., 23, 682 (1983).

226. C. LEONARD, J.L. HALARY, L. MONNERIE, D. BROUSSOUX, B. SERVET and F. MICHERON, Polym. Comm., 24, 110 (1983).

227. A.K. MUKHERJI, M.A. BUTLER and D.L. EVANS, J. Appl. Polym. Sci., 25, 1145 (1980).

228. J.L. KOENIG and M.J.M. TOVAR-RODRIGUEZ, Appl. Spectrosc., 35, 543

(1981).

229. L.H. WANG and R.S. PORTER, J. Polym. Sci., Polym. Phys. Ed., 21, 1815 (1983).

230. D.F. VARNELL, J.P. RUNT and M.M. COLEMAN, Macromolecules, 14, 1350 (1981).

231. M.M. COLEMAN, D.F. VARNELL and J.P. RUNT, Contemp. Topics Polym. Sci., 4, 807 (1984).

232. A.W. BIRLEY and X.Y. CHEN, Brit. Polym. J., 16, 77 (1984).

233. M.M. COLEMAN and E.J. MOSKALA, Polymer, 24, 251 (1983).

234. A. GARTON, NRCC/IMRI symposium, "Polyblends-'83", Montreal, Que. Canada, April 12, 1983; Polym. Eng. Sci., 24, 112 (1984).

235. E.J. MOSKALA and M.M. COLEMAN, Polym. Comm., 24, 206 (1983).

236. A. GARTON, Polym. Eng. Sci., 23, 663 (1983).

237. D.J. BURCHELL, J.E. LASCH, R.J. FARRIS and S.L. HSU, Polymer, 23, 965 (1982).

238. D.J. BURCHELL and S.L. HSU, A.C.S., Adv. Chem. Ser., 203, 533 (1983).

239. F.J. LU, D.J. BURCHELL, X. LI and S.L. HSU, Polym. Eng. Sci., 23, 861 (1983).

240. F.J. LU, E. BENEDETTI and S.L. HSU, Macromolecules, 16, 1525 (1983).

241. S.L. HSU, L.D. COYNE, D.J. BURCHELL, X. LI and F.J. LU, 16th Europhysics Conf. Macromol. Phys., June 4-7, 1984, Brugge, Belgium.

242. S.R. FAHRENHOLTZ and T.K. KWEI, Macromolecules, 14, 1076 (1981).

243. M.M. COLEMAN and D.F. VARNELL, Macromolecules, 15, 937 (1982).

244. S.R. FAHRENHOLTZ, Macromolecules, 15, 937 (1982).

245. T.K. KWEI, E.M. PEARCE and B.Y. MIN, Proc. 28th IUPAC, Macromol. Symp.,

1982 Amherst, MA, July 12-16 (1982).

246. M. MIYA, R. IWAMOTO and S. MIMA, J. Polym. Sci., Polym. Phys. Ed., 22, 1149 (1984).

247. E. BALIZER and H. TALAAT, J. Phys., C6, 131 (1983).

248. A. GARTON, NRCC/IMRI symposium "Composites-'83", Boucherville, Que. Canada, Nov. 29, 1983; Polym. Compos., 5, 258 (1984).

249. A. GARTON and J.H. DALY, Canadian Aeronautics Space Inst. Conf., Ottawa, Ont. Canada, June 1984.

250. G.D. PATTERSON, A.C.S., Adv. Chem. Ser., 176, 529 (1979).

251. M.M. COLEMAN, D.J. SKROVANEK and P.C. PAINTER, Appl. Spectr., 38, 448 (1984).

252. D. YANG, B. ZHANG, Y. YANG, Zh. FANG, G. SUN and Zh. FENG, Polym. Eng. Sci., 24, 612 (1984).

253. G. LARS, J. BOHSE, R. STEPHAN and J. SACHSE, Plast. Kautsch., 30, 458 (1983).

254. C.B.-S. WANG, PhD thesis, Univ. Wisconsin, Madison, WI (1982).

255. M. JIANG, X.-Y. HUANG and T.-Y. YU, Polymer, 24, 1259 (1983).

256. M. TAKAYANGI and K. GOTO, J. Appl. Polym. Sci., 29, 2547 (1984).

257. D.L. HANDLIN, W.J. MacKNIGHT, and E.L. THOMAS, Macromolecules, 14, 795 (1980).

258. M.A. TUNG and L.J. JONES, Scanning Electron Microscopy, 3, 523 (1981).

259. M.M. DUMOULIN and L.A. UTRACKI, C.R.G. Colloquium, "Characterization of Plastics and Rubbers", Hamilton, Ont. Canada, 21-22 June (1984); C.S.Ch.E. Annual Meeting, Quebec, Canada 30 Sept. - 3 Oct. (1984).

260. M.M. DUMOULIN, L.A. UTRACKI and P.J. CARREAU, 36th Canadian Chem. Eng.

Conf. Sarnia, Ont. Canada, 5-8 Oct (1986); 2nd Conf. European Rheol., Prague, ČSR, 17-20 June (1986).

261. L.A. UTRACKI, M.M. DUMOULIN and P.J. CARREAU, S.P.E., Techn. Papers, 33, 1419 (1987).

262. C.B. BUCKNALL, D. CLAYTON and W.E. KEAST, J. Mater.Sci., 7, 1443 (1972); ibid. 8, 514 (1973).

263. C.B. BUCKNALL and I.C. DRINKWATER, J. Mater. Sci., 8, 1800 (1973).

264. C.B. BUCKNALL, "Toughened Plastics", Appl. Sci. Publ., London, UK (1977).

265. C.B. BUCKNALL and W.W. STEVENS, J. Mater. Sci., 15, 2950 (1980).

266. C.B. BUCKNALL and C.J. PAGE, J. Mater. Sci., 17, 808 (1982).

267. C.B. BUCKNALL and I.K. PARTRIDGE, Polymer, 24, 639 (1983).

268. C.B. BUCKNALL, P. DAVIES and I.K. PARTRIDGE, Polymer, 26, 109 (1985).

269. C.B. BUCKNALL and I.K. PARTRIDGE, NRCC/IMRI symposium "Polyblends-'85", Boucherville, Que. Canada, 16 and 17 April, 1985; Polym. Eng. Sci., 26, 54 (1986).

270. S.Y. HOBBS, NRCC/IMRI Symposium "Polyblends-'85", Boucherville, Que. Canada, 16 and 17 April 1985; Polym. Eng. Sci., 26, 74 (1986).

271. B.A. THORTON, R.G. VILLASENOR and B. MAXWELL, J. Appl. Polym. Sci., 25, 653 (1980).

272. G.M. JORDHAMO, J.A. MANSON and L.H. SPERLING, Polym. Eng. Sci., 26, 517 (1986).

273. K.M. HONG and J. NOOLANDI, Macromolecules, 14, 727 (1981); ibid., 14, 1229 (1981).

274. J. NOOLANDI and K.M. HONG, Macromolecules, 15, 482 (1982).

275. J. NOOLANDI, NRCC/IMRI symposium "Polyblends-'83", Montreal, Que. Canada, April 12, 1983; Polym. Eng. Sci., 24, 70 (1984).

276. R. FAYT, R. JÉRÔME and PH. TEYSSIÉ, J. Polym. Sci., Polym. Lett. Ed., 19, 79 (1981); 24, 25 (1986).

277. R. FAYT, R. JÉRÔME and PH. TEYSSIÉ, J. Polym. Sci., Polym. Phys. Ed., 19, 1269 (1981); 20, 2209 (1982);

278. R. FAYT, R. JÉRÔME and PH. TEYSSIÉ, Macromol., Chem., 187, 837 (1986).

289. R. FAYT and PH. TEYSSIÉ, Macromolecules, 199, 2077 (1986).

290. T. OUHADI, R. FAYT, R. JÉRÔME and PH. TEYSSIÉ, J. Polym. Sci., Polym. Phys. Ed., 24, 973 (1986); J. Appl. Polym. Sci., 32, 5647 (1986).

291. B. ALBERT, R. JÉRÔME, PH. TEYSSIÉ and D. BAEYENS-VOLANT, J. Polym. Sci, Polym. Chem. Ed., 24, 537, 551, 2577 (1986).

292. T. OUHADI, R. FAYT, R. JÉRÔME and PH. TEYSSIÉ, Polym. Commun., 27, 212 (1986).

293. R.E. COHEN and A.R. RAMOS, Macromolecules, 12, 131 (1979).

294. W.J. COUMANS, D. HEIKENS and S.D. SJOERDSMA, Polymer, 21, 103 (1980).

295. A. GHAFFAR, C. SADRMOHAGHEGH and G. SCOTT, Eur. Polym. J., 17, 941 (1981).

296. C. SADRMOHAGHEGH, G. SCOTT and E. SETOUDEH, Eur. Polym. J., 19, 81 (1983).

297. R.E. COHEN and D.E. WILFONG, Macromolecules, 15, 370 (1982).

298. M.A. HARNEY and R.E. COHEN, O.N.R. Technical Report No. 10, Aug. 22, 1983; AD-A132-832.

299. E.B. TROSTYANSKAYA, M.B. ZEMSKOV and Ya. MIKHASENOK, Plast. Massy, 11, 28 (1983).

300. J.I. EGUIAZABAL, J.J. IRUIN, M. CORTAZAR and G.M. GUZMAN, J. Appl. Polym. Sci., 32, 5945 (1986).

301. R.A. MENDLESON, J. Polym. Sci., Polym. Phys Ed., 23, 1975 (1985).

302. L.G. BOURLAND and D.M. BRAUNSTEIN, J. Appl. Polym Sci., 32, 6151 (1986).

303. J.M. WEFER, U.S. Pat. No. 4,493,921 (Jan. 15, 1985), to Uniroyal Inc.

304. K. YAMADA, M. UCHIDA and M. TAKAYONAYI, J. Appl. Polym. Sci., 32, 5231 (1986).

305. L.H. SPERLING, "Interpenetrating Polymer Networks and Related Materials", Plenum Press, New York (1981).

306. L.H. SPERLING, Mod. Plast., 58, 74 (1981).

307. D.L. SIEGFRIED, D.A. THOMAS and L.H. SPERLING, J. Appl. Polym. Sci., 26, 177 (1981); Polym. Eng. Sci., 21, 39 (1981).

308. H. DJOMO, R. COLMENARES and G.C. MEYER, Eur. Polym. J., 17, 521 (1981).

309. H. ADACHI, S. NISHI and T. KOTAKA, Polym. J. (Tokyo), 14, 985 (1982).

310. L.H. SPERLING and J.M. WIDMAIER, Polym. Eng. Sci., 23, 693 (1983).

311. J.K. YEO, L.H. SPERLING and D.A. THOMAS, Polymer, 24, 307 (1983).

312. L.H. SPERLING, J.M. WIDMAIER, J.K. YEO and J. MICHEL, Polym. Sci. Technol., 20, 191 (1983).

313. L.H. SPERLING, S.P.E., Techn. Papers, 30, 474 (1984).

314. D.L. SIEGFRIED, PhD thesis, Lehigh Univ., Bethlehem, PA (1980).

315. E. HAGE Jr., PhD thesis, North Carolina State Univ., Raleigh (1983).

316. S. KRAUSE, 5th Conveg. Ital. Sci. Macromol., pgs. 117-24 (1981).

317. D.R. PAUL in ref. [14].

318. J.W. BARLOW and D.R. PAUL, Polym. Eng. Sci., 24, 525 (1984).

319. T.D. TRAUGOTT, J.W. BARLOW and D.R. PAUL, J. Appl. Polym. Sci., 28, 2947 (1983).

320. H.W. STARKWEATHER, Jr., Macromolecules, 13, 892 (1980).

321. M. KIMURA, R.S. PORTER and G. SALEE, Amer. Chem. Soc., Org. Coating Plast. Chem. Prepr.,45, 84 (1981); J. Polym. Sci., Polym. Phys. Ed., 21, 367 (1983).

322. M. KIMURA, G. SALEE and R.S. PORTER, J. Appl. Polym. Sci., 29, 1629 (1984).

323. J.I. EGUIAZABAL, M.E. CALAHORRA, M.M. CORTAZAR and J.J. IRUIN, Polym. Eng. Sci., 24, 608 (1984).

324. J. DEVAUX, P. GODDARD and J.P. MERCIER, J. Polym. Sci., Polym. Phys. Ed., 20, 1875, 1895, 1901 (1982).

325. J. DEVAUX, P. GODARD, J.P. MERCIER, R. TOUILLAUX and J.M. DEREPPE, J. Polym. Sci., Polym. Phys. Ed., 20, 1881 (1982).

326. J. DEVAUX, 16th Europhysics Conf. Maromol. Phys., June 4-7, 1984, Burgge, Belgium.

327. L.Z. PILLON and L.A. UTRACKI, NRCC/IMRI symposium "Polyblends-'84", April 17, 1984; Polym. Eng. Sci., 24, 1300 (1984); 3rd Intl. Conf. "Reactive Processing of Polymers", Sept. 5-7, 1984 Stasbourg, France; Polym. Process Eng., 3, 375 (1986); NRCC/IMRI symposium "Polyblends-'85", Boucherville, Que. Canada, April 16, 1985.

328. L.M. ROBESON, U.S. Pat. No. 4,324,869 (Apr. 13, 1982) to Union Carbide.

329. J. COQUARD and J. GOLETTO, U.S. Pat. No. 4,346,024 (Aug. 24, 1982) to Rhone-Poulenc.

330. F. KUNIO and K. HIDEO, Europ. Pat. 44,730 (July 15, 1981) to Asahi-Dow.

331. R.L. DIECK and R.J. KOSTELNIK, Europ. Pat. 71,773 (July 7, 1982) to General Electric.

332. M.J. ROURA, U.S. Pat. No. 4,346,194 (Apr. 24, 1982) to DuPont.

333. T. KOTAKA and H. WATANABE, in "Current Topics in Polymer Science", R.M. Ottenbrite, L.A. Utracki and S. Inoue, Eds., Hanser Publ., München, FRG (1987).

334. G. HADZIIOANNU, PhD thesis, Univ. L. Pasteur, Strasbourg, France (1980).

335. S. WU in ref. [14].

335. E. HELFAND and A.M. SAPSE, J. Chem. Phys., 62, 1327 (1975).

336. J.F. JOANNY and L. LEIBLER, J. Physique, 39, 951 (1978).

337. L. LEIBLER, Macromolecules, 15, 1283 (1982).

338. C.I. POSER and I.C. SANCHEZ, Macromolecules, 14, 361 (1981).

339. C.I. POSER and I.C. SANCHEZ, J. Colloid. Interf. Sci., 69, 539 (1979).

340. I.C. SANCHEZ, NRCC/IMRI symposium "Polyblends-'83", Montreal, Que. Canada, April 12, 1983; Polym. Eng. Sci., 24, 79 (1984).

341. I.C. SANCHEZ, Polym. Eng. Sci., 24, 598 (1984).

342. J.W. CAHN in "Segregation to Interfaces", J.J. Blakely and W.C. Johnson, Eds., A.S.M. Semin. Ser., Cleveland (1978).

343. I.M. LIFSCHITZ and V.V. SLYOZOV, J. Chem. Solids, 19, 35 (1961).

344. F.R. EIRICH, "Rheology: Theory and Application", Academic Press, New York (1956); five volumes.

345. A.S. LODGE, "Elastic Liquids", Academic Press, New York (1964).

346. B.D. COLEMAN, H. MARKOVITZ and W. NOLL, "Viscometric Flows of Non-Newtonian Fluids", Springer-Verlag, New York (1966).

347. S. MIDDLEMAN, "The Flow of High Polymers", Interscience Publ., New York

(1968).

348. G. ASTARITA and G. MARRUCCI, "Principles of Non-Newtonian Fluid Mechanics", McGraw-Hill, London (1974).

349. J.L. LEBLANC, "Rhéologie Expérimentale des Polymères à l'Etat Fondu", Editions CEBEDOC, 2 rue A. Stévart, Liège, Belgium (1974).

350. R. DARBY, "Viscoelastic Fluids", M. Dekker, New York (1976).

351. L.E. NIELSEN, "Polymer Rheology", M. Dekker, New York (1977).

352. J. HARRIS, "Rheology and non-Newtonian Flow", Longman, London (1977).

353. R.B. BIRD, R.C. ARMSTRONG and O. HASSAGER, "Dynamics of Polymeric Liquids: Volume 1, Fluid Mechanics"; R.B. BIRD, O. HASSAGER, R.C. ARMSTRONG and C.F. CURTIS, "Dynamics of Polymeric Liquids: Volume 2, Kinetic Theory". John Wiley & Sons, New York (1977).

354. W.B. SCHOWALTER, "Mechanics of Non-Newtonian Fluids", Pergamon Press, Elmsford, New York (1978).

355. R.S. LENK, "Polymer Rheology", Applied Science Publishers Ltd., London (1978).

356. C.J.S. PETRIE, "Extensional Flows", Pittman, London (1979).

357. J.D. FERRY, "Viscoelastic Properties of Polymers", 3rd Ed., John Wiley & Sons, New York (1980).

358. J.A. BRYDSON, "Flow Properties of Polymer Melts", Godwin, London (1981).

359. G.V. VINOGRADOV and A. Ya. Malkin, "Polymer Rheology", Khimya, Moscow (1977). [English translation by G.V. Vinogradov, Springer-Verlag, Berlin, New York (1981)].

360. H. JANESCHITZ-KRIEGL, "Polymer Melt Rheology and Flow Birefringence", Springer-Verlag, Berlin (1983).

361. J.R. VAN WAZER, J.W. LYONS, K.Y. KIM and R.E. COLWELL, "Viscosity and Flow Measurements", Intersci. Publ., New York (1963).

362. PH. SHERMAN, "Industrial Rheology", Academic Press, London (1970).

363. K. WALTERS, "Rheometry", Chapman & Hall, London (1975).

364. C.D. HAN, "Rheology in Polymer Processing", Academic Press, New York (1976).

365. VDI-Gesellschaft Kunststofftecknik, "Praktische Rheologie der Kunststoffe", VDI-Verlag, Duesseldorf (1978).

366. R.W. WHORLOW, "Rheological Techniques", Ellis Horwood (distributed by John Wiley & Sons), New York (1979).

367. F.N. COGSWELL, "Polymer Melt Rheology: A Guide for Industrial Practice", G. Godwin, London (1981).

368. C.D. HAN, "Multiphase Flow in Polymer Processing", Academic Press, New York (1981).

369. J. M. DEALY, "Rheometers for Molten Plastics: A Practical Guide to Testing and Property Measurement", Van Nostrand Reinhold, New York (1982).

370. P. AVENAS, J.-F. AGASSANT and J.-PH. SERGENT, "La Mise en Forme des Matières Plastiques", Lavoisier, Paris (1982).

371. A.I. MALKIN, "Experimental Methods of Polymer Physics: (Measurement of Mechanical Properties, Viscosity, and Diffusion)", Prentice-Hall Englewood Cliffs, NJ (1983).

372. R. TANNER, "Engineering Rheology", Clarendon Press, Cambridge UK (1985).

373. A.A. COLLYER and D.W. CLEGG, Eds., "The Physical Principles of Rheological Measurements", Elsevier Sci. Publ., London (1987).

374. L.A. UTRACKI, in "Current Topics in Polymer Science", R.M. Ottenbrite, L.A. Utracki and S. Inoue, Eds., Hanser Publ., München, FRG (1987).

375. L.A. UTRACKI, in ref. [373].

376. J.M. DEALY, J. Rheol., 28, 181 (1984).

377. E. SCHALEK and A. SZEGVARY, Kolloid Z., 32, 318 (1923).

378. C.C. MILL, Ed.; "Rheology of Dispersed Systems," Pergamon Press, London (1959).

379. P. SHERMAN, Ed., "Emulsion Science," Academic Press, London (1968).

380. P. SHERMAN, Ed., "Rheology of Emulsions," Pergamon Press, Oxford (1963).

381. W.A. BAUER and E.A. COLLINS, in Vol. 4, ref. [344].

382. D.J. JEFFREY and A. ACRIVOS, AIChE J., 22, 417 (1976).

383. J. MEWIS, J. Non-Newtonian Fluid Mech., 6, 1 (1979).

384. L.A. UTRACKI and B. SCHLUND, Polym. Eng. Sci., 27, 367 (1987).

385. B. SCHLUND, and L.A. UTRACKI, NRCC/IMRI Symposium "Polyblends-'87", Boucherville, Que. Canada, 28-29 April, 1987; Polym, Eng. Sci., 28, 000 (1988).

386. M.M. DUMOULIN, PhD thesis, École Polytechnique, Montréal (1987).

387. L.A. UTRACKI and G.L. BATA, "Polymer Alloys", CANPLAST meeting, Montreal, October 25, (1981); Matériaux Techn., 70, 223, 290 (1982).

388. L.A. UTRACKI and M.R. KAMAL, " Polyblends-81" symposium, NRCC/IMRI Montreal, April 1981; Polym. Eng. Sci., 22, 96 (1982).

389. L.A. UTRACKI, NATEC, Bal Harbour, Florida, October 25-27, 1982; Polym. Eng. Sci., 23, 602 (1983).

390. L.A. UTRACKI, Polym-Plast. Technol. Eng., 22, 27 (1984).

391. S. GLASSTONE, K.L. LAIDLER and H. EYRING, "Theory of Rate Processes",

McGraw-Hill, New York (1967).

392. A. BONDI, in Vol 4., ref. [344].

393. J.P. MONFORT, G. MORIN, J. ARMAN and Ph. MONGE, Polymer, 19, 277 (1978).

394. S.F. CHRISTOV, I.I. SKOROKHODOV and Z.V. SHURALAVA, Vysokomol. Soed., A20, 1699 (1978).

395. A. FRANK and J. MEISSNER, Rheol. Acta, 23, 117 (1984).

396. R. SIMHA and T. SOMCYNSKY, Macromolecules, 2, 342 (1969).

397. J.E. MCKINNEY and R. SIMHA, Macromolecules, 9, 430 (1976).

398. O. OLABISI and R. SIMHA, J. Appl. Polym. Sci., 21, 149 (1977).

399. R.K. JAIN and R. SIMHA, J. Chem. Phys., 72, 4909 (1980).

400. R.K. JAIN and R. SIMHA, Macromolecules, 13, 1501 (1980).

401. R. SIMHA, Polym. Eng. Sci., 22, 74 (1982).

402. R. SIMHA and R.K. JAIN, Polym. Eng. Sci., 24, 1284 (1984).

403. L.A. UTRACKI and R. SIMHA, A.C.S., Polym. Prepr., 23(2), 67 (1982).

404. L.A. UTRACKI, Canad. J. Chem. Eng., 61, 753 (1983).

405. L.A. UTRACKI, Polym. Eng. Sci., 23, 446 (1933); 25, 655 (1985).

406. L.A. UTRACKI, A.C.S., Polym. Prepr., 24(2), 113 (1983).

407. L.A. UTRACKI, J. Rheol., 30, 829 (1986).

408. N.P. SUPRUN and O.V. ROMANKEVICH, Khim, Tekhnol. (Kiev), 2, 29 (1984).

409. E. MARTUSCELLI, L. VICINI and A. SEVES, Macromol. Chem., Rapid Commun., 5, 255 (1984).

410. Y.P. SINGH and R.P. SINGH, J. Appl. Polym. Sci., 29, 1653 (1984).

411. Y. AOKI, Polym. J., 16, 431 (1984).

412. W.M. PREST, Jr. and R.S. PORTER, J. Polym. Sci., Part A-2, 10, 1639 (1972).

413. R. GENILLON and J.F. MAY, 5th Conf. Europ. Plast. Caoutch., Paris (1978).

414. R. FUJIMURA and K. TWAKURA, Int. Chem. Eng., 10, 683 (1970); Kobunshi Ronbunshu, 31, 617 (1974).

415. M.H. DOAN and J. BRUNET, Ing. Eng. Chem. Fundam., 11, 356 (1972); J. BRUNET and K.E. GUBBINS, Trans. Faraday Soc., 65, 1255 (1969).

416. G.D. KIRIANOV, R.M. VASENIN and B.N. DINZBURG, Vysokomol. Soed., B17, 492 (1975).

417. R. SIMHA, J. Appl. Phys., 23, 1020 (1952).

418. M. MOONEY, J. Colloid Sci., 6, 162 (1951).

419. L.A. UTRACKI and B. FISA, Polym. Compos., 3, 193 (1982).

420. L.A. UTRACKI, J. Macromol. Sci. Phys., B18, 725 (1980).

421. L.A. UTRACKI and R. SIMHA, J. Rheol., 25, 329 (1981).

422. D.G. THOMAS, J. Colloid Sci., 20, 267 (1965).

423. L.A. UTRACKI, B.D. FAVIS and B. FISA, Polym. Compos., 5, 277 (1984).

424. M.M. CROSS, A. KAYE, J.L. STANFORD, and R.F.T. STEPTO, A.C.S., Polym. Mater. Sci. Eng. Div. Preprints, 49, 531 (1983).

425. B. FISA and L.A. UTRACKI, Polym. Compos., 5, 36 (1984).

426. L.A. UTRACKI, Rubber Chem. Technolog., 57, 507 (1984).

427. H. BRENNER and D.W. CONDIFF, J. Colloid Interface Sci., 47, 199 (1979).

428. M. DOI and S.F. EDWARDS, J. Chem. Soc., Faraday Trans. II, 74, 560, 918 (1978).

429. I.M. KRIEGER and T.J. DOUGHERTY, Trans. Soc. Rheol., 3, 137 (1959).

430. H.L. GOLDSMITH and S.G. MASON, in Vol 4, ref. [344].

431. T.L. SMITH, J. Paint Technol., 44, 71 (1972).

432. A. ZOSEL, Rheol. Acta, 21, 72 (1982).

433. R.J. HUNTER, R. MATARESE and D.H. NAPPER, Colloid Surf., 7, 1 (1983).

434. C.R. WILDEMUTH and M.C. WILLIAMS, Rheol. Acta, 23, 627 (1984).

435. J.T. LIN, M.S. EL-AASSER, C.A. SILEBI and J.W. VANDERHOFF, J. Colloid Interface Sci., 110, 305 (1986).

436. Y. MIKAMI, Nihon Reor. Gakk., 8, 3, 137 (1980).

437. G.K. BATCHELOR, J. Fluid Mech., 44, 419 (1970); ibid., 46, 813 (1971).

438. T.E. KIZIOR and F.A. SEYER, Trans Soc. Rheol., 18, 271 (1974).

439. G.B. WEINBERGER and J.D. GODDARD, Int. J. Multiphase Flow, 1, 465 (1974).

440. J. MEWIS and A.B. METZNER, J. Fluid Mech., 62, 593 (1974).

441. G.J. LIN, J.H. PERRY and W.R. SCHOWALTER, J. Fluid Mech., 44, 1 (1970).

442. E.J. HINCH and L.G. LEAL, J. Fluid Mech., 52, 683 (1972).

443. W.E. VANARSDALE, J. Rheol., 26, 477 (1982).

444. C.N. DESILVA, Acta Mech., 47, 7 (1982); 49, 221 (1983).

445. M.A. BIBBO, S.M. DINH and R.C. ARMSTRONG, J. Rheol., 29, 905 (1985).

446. J.C. OLDROYD, Proc. Roy. Soc., A218, 122 (1953); A232, 5676 (1955).

447. M.A. NAWAB and S.G. MASON, Trans. Faraday Soc., 54, 1712 (1958).

448. S. MATSUMOTO and P. SHERMAN, J. Colloid Interface Sci., 30, 525 (1969).

449. L.A. UTRACKI, Gulf Oil Canada internal reports (1970) and (1971).

450. A. BRANDT and G. BUGLIARELLO, Trans. Soc. Rheol., 10, 229 (1966).

451. O. OKAGAWA and S.G. MASON, Can. J. Chem., 53, 2689 (1975).

452. J.B. HARRIS and J.F.T. PITTMAN, Trans. Inst. Chem. Eng., 54, 73 (1976).

453. D.C. ALLPORT and W.H. JONES, Eds., "Block Copolymers", Appl. Sci. Publ, London (1973).

454. R.J. CERESA, Ed., "Block and Graft Copolymerization", J. Wiley and Sons, London (1973).

455. A. NOSHAY and J.E. MCGRATH, "Block Copolymers; Overview and Critical Survey", Academic Press, New York (1977).

456. M.J. FOLKES, Ed., "Processing, Structure and Properties of Block Copolymers", Elsevier Appl. Sci. Publ., London (1985).

457. T. KOTAKA and H. WATANABE, in "Current Topics in Polymer Science", R.M. Ottenbrite, L.A. Utracki and S. Inoue, Eds., Hanser Publ., München, FRG (1987).

458. G. KRAUS and J.T. GRUVER, J. Appl. Polym. Sci., 11, 2121 (1967).

459. G. HOLDEN, E.T. BISHOP and N.R. LEGGE, J. Polym, Sci., C26, 37 (1969).

460. G.M. ESTES, S.L. COOPER and A.V. TOBOLSKY, J. Macromol. Chem., C4, 313 (1970).

461. K.R. ARNOLD and D.J. MEIER, J. Appl. Polym. Sci., 14, 427 (1970).

462. F.N. COGSWELL and D.E. HANSON, Polymer, 16, 936 (1975).

463. C.I. CHUNG and J.C. GALE, J. Polym. Sci. Phys. Ed., 14, 1149 (1976).

464. N.V. CHII, A.I. ISAYEV, A. Ya. MALKIN, G.V. Vinogradov and I.Yu. Kirchevskaya, Polym. Sci. URSS, 17, 983 (1975).

465. E.R. PICO and M.C. WILLIAMS, Nature, 259, 388 (1976).

466. C.P. HENDERSON and M.C. WILLIAMS, J. Polym. Sci., Polym. Lett. Ed., 17, 257 (1979).

467. T.Y. LIU, D.S. SOONG and D. DEKEE, Chem. Eng. Commun., 22, 273 (1983).

468. G. HOLDEN, Chapter 6 in [62].

469. M.L. WILLIAMS, R.F. LANDEL and J.D. FERRY, J. Amer. Chem. Soc., 77, 3701 (1955).

470. D.F. LEARY and M.C. WILLIAMS, J. Polym. Sci. B, 8, 335 (1970); J. Polym. Sci., Phys. Ed., 11, 354 (1973); ibid 12, 265 (1974).

471. J. LYNGAAE-JORGENSEN in ref. [456].

472. J. LYNGAAE-JORGENSEN and K. SONDERGAARD, NRCC/IMRI Symposium, "Polyblends -'86", Montreal, Que. Canada, April 4, 1986; Polym. Eng. Sci., 27, 344, 351 (1987).

473. O.V. ROMAKEVICH, T.I. ZHILA, S.E. ZABELLO, N.A. SKLYAR and S. Ya FRENKEL, Vysokomol. Soed., A24, 2282 (1982).

474. L.S. BOLOTNIKOVA, A.K. EVSEER, Yu.N. PANOV and S.Ya. FRENKEL, Vysokomol. Soed., B24, 154 (1982).

475. T.I. ABLAZOVA, M.V. CEBRENKO, A.B.V. YUDIN, G.V. VINOGRADOV and B.V. YARLYKOV, J. Appl. Polym. Sci., 19, 1781 (1975).

476. M.V. CEBRENKO, A.I. BENZAR, A.V. YUDIN and G.V. VINOGRADOV, Vysokomol. Soed., A21, 830 (1979).

477. T.I. ZHILA, V.I. MAZURENKO, O.V. ROMANKEVICH, S.E. ZABELLO and V.V. ANOKHIN, Khim. Tekhnol. (Kiev), 5, 35 (1980).

478. V. DOBRESCU, Polym. Bull., 5, 75 (1981).

479. D. CURTO, F.P. LAMANTIA and D. ACIERNO, Rheol. Acta, 22, 197 (1983).

480. K. HAYASHIDA, J. TAKAHASHI and M. MATSUI, Intl. Congress Rheol., Tokyo, 1968; S. Onogi, Ed., Univ. Tokyo Press, 4, 525 (1970).

481. C.D. HAN and T.C. YU, J. Appl. Polym. Sci., 15, 1163, 2579 (1971); Polym. Eng. Sci., 12, 81 (1972).

482. H.-K. CHUANG and C.D. HAN, Ch. 11 in ref. [21]; J. Appl. Polym. Sci., 29, 2205 (1984).

483. K. DIMOV and M. SAVOV, Vysokomol. Soed., A22, 65 (1980).

484. J.F. CARLEY and S.C. CROSSAN, S.P.E., Techn. Papers, 26, 285 (1980); Polym. Eng. Sci., 21, 249 (1981).

485. Yu.S. LIPATOV, A.Ye. NESTEROV, T.D. IGNATOVA, V.F. SHUMSKII and A.N. GORBATENKO, Vysokomol. Soed., A24, 549 (1982).

486. Yu.S. LIPATOV, Mekh. Kompoz. Mater., 3, 499 (1983).

487. V.N. KULEZNEV, O.L. MELNIKOVA, V.D. KLYKOVA, V.P. SKORTSOV and V.S. GLUKHOVSKOI, Kalloid, Zh. 37, 273 (1975).

488. A.P. PLOCHOCKI, Polimery, 26, 261 (1981).

489. Yu.S. LIPATOV, V.P. Shumskii, Ye.V. Lebedev and A.Ye. Nesterov, Dolk. Akad. Nauk SSSR, 244, 148 (1979).

490. A.N. GORBATENKO, T.D. IGNATOVA, V.F. SHUMSKII, A.Ye. NESTEROV, Yu.S. LIPATOV, L.S. BOLOTNIKOVA and Yu.N. PANOV, Kompoz. Polim. Mater., 15, 18 (1982).

491. C.-C. LIN, Polym. J., 11, 185 (1979).

492. Yu.S. LIPATOV, E.V. LEBEDEV and V.F. SHUMSKII, Dopov. Akad. Nauk URSR, Ser. B, 1983, (9), 39.

493. L.A. UTRACKI, 74th annual meeting of the AIChE; Los Angeles, CA, November 15-18, 1982.

494. N.Q. DZUY and D.V. BOGER, J. Rheol., 27, 321 (1983); ibid., 29, 335 (1985).

495. D.C.-H. CHENG, Rheol. Acta, 25, 542 (1986).

496. K.A. MAZICH, PhD thesis, Northwestern Univ., Evanston Illinois (1983).

497. T. AMARI and K. WATANABE, Polym. Eng. Reviews, 3, 277 (1983).

498. L.A. UTRACKI, A. CATANI, G.L. BATA, M.R. KAMAL and V. TAN, J. Appl. Polym. Sci., 27, 1913 (1982).

499. L.A. UTRACKI, G.L. BATA, V. TAN and M.R. KAMAL, Preprints of the 2nd World Congress of Chemical Engineering, Montreal, Quebec, October 5, 1981, 6, 428 (1981).

500. L.A. UTRACKI, M.M. DUMOULIN and P. TOMA, NRCC/IMRI symposium "Polyblends-'85", Boucherville, Que., Canada. April 16-17, 1985; Polym. Eng. Sci., 26, 37 (1986).

501. M.M. DUMOULIN, P. TOMA, L.A. UTRACKI, I. JINNAH and M.R. KAMAL, S.P.E., Techn. Papers, 31, 534 (1985).

502. C.K. SHIH, Polym. Eng. Sci., 16, 198 (1976).

503. C.K. SHIH, in "Science and Technology of Polymer Processing", N.P. Suh and N.-H. SUNG, Eds., MIT Press, Cambridge, MA (1979).

504. R.C. KANU and M.T. SHAW, Polym. Eng. Sci., 22, 507 (1982).

505. M. NISHI, H. WATANABE and T. KOTAKA, Nihon Reor., Gakk., 9, 23 (1981).

506. C. WISNIEWSKI, G. MARIN and Ph. MONGE, Eur. Polym. J., 21, 479 (1985).

507. C. BELARIBI, G. MARIN and Ph. MONGE, Eur. Polym. J., 22, 481, 487 (1986).

508. A.P. PLOCHOCKI, NRCC/IMRI symposium "Polyblends-'82", Montreal, Que., Canada, April 20, 1982; Polym. Eng. Sci., 22, 1153 (1982).

509. K. MIN, PhD thesis, Univ. Tennesse, Knoxville, TN (1984).

510. L.A. UTRACKI, G.L. BATA, V. TAN and M.R. KAMAL, Preprints of the 2nd World Congress of Chemical Engineering, Montreal, Quebec, October 5, 1981; 6, 428 (1981).

511. V.Ye. DREVAL, A. KASSA, Ye.K. BORISENKOVA, M.L. KERBER, G.V. VINOGRADOV and M.S. AKUTIN, Vysokomol. Soed., A25, 156 (1983).

512. M.M. DUMOULIN, C. FARHA and L.A. UTRACKI, NRCC/IMRI symposium, "Polymer

Blends-'84", Boucherville, Que., Canada, April 17, 1984, Polym. Eng. Sci., 24, 1319 (1984).

513. Y. LIPATOV, J. Appl. Polym. Sci., 22, 1895 (1978).

514. L.A. UTRACKI and G.L. BATA, in " Polymer Alloys III", D. Klemper and K.C. FRISCH, Eds., Plenum Press, New York (1982).

515. L.A. UTRACKI, Adv. Polym. Technol., 5, 41 (1985).

516. R.I. TANNER, J. Polym. Sci., A-2, 8, 2067 (1970).

517. L.A. UTRACKI, M.R. KAMAL and Z. BAKERDJIAN, J. Appl. Polym. Sci., 19, 487 (1975).

518. J.L. LEBLANC, Rubb. Chem. Technol., 54, 905 (1981).

519. O.V. ROMANKEVICH and S.Y. FRENKEL, Kompoz. Polim. Mater., 14, 6 (1982).

520. O.V. ROMANKEVICH, K.V. YAKOVLEV, S.E. ZABELLO, T.I. ZHILA and V.S. RUDCHUK, Khim. Volokna, 1, 21 (1984).

521. F.P. LAMANTIA, D. CURTO and D. ACIERNO, Acta Polym., 35, 71 (1984).

522. D. ACIERNO, D. CURTO, F.P. LAMANTIA and A. VALENZA, NRCC/IMRI symposium "Polyblends-'85", Boucherville, Québec, Canada, April 16-17, 1985; Polym. Eng. Sci., 26, 28 (1986).

523. F. DERI, R. GENILLON and J.F. MAY, Angew, Makromol. Chem., 134, 11 (1985).

524. A. SANTAMARIA, M.E. MUNOZ, J.J. PENA and P. REMIRO, Angew, Makromol. Chem., 134, 63 (1985).

525. L.A. UTRACKI, M.R. KAMAL and N.M. AL-BASTAKI, S.P.E. Techn. Papers, 30, 417 (1984).

526. F.P. LAMANTIA, D. ACIERNO and D. CURTO, Rheol. Acta, 21, 452 (1982).

527. M.M. DUMOULIN, L.A. UTRACKI and J. LARA, NRCC/IMRI symposium

"Polyblends-'83", Montreal, Quebec, Canada, April 12, 1983; Polym. Eng. Sci., 24, 117 (1984).

528. B. SCHLUND and L.A. UTRACKI, Polym. Eng. Sci., 27, 359, 380 (1987).

529. S. ENDO, K. MIN. J.L. WHITE and T. KYU, NRCC/IMRI symposium "Polyblends-'85", Boucherville, Quebec, Canada, April 16 and 17, 1985; Polym. Eng. Sci., 26, 45 (1986).

530. K. MIN. J.L. WHITE and J.F. FELLERS, NRCC/IMRI symposium "Polyblends-'84", Boucherville, Quebec, Canada, April 17, 1984; Polym. Eng. Sci., 24, 1327 (1984).

531. H. SUGIYAMA, D.N. LEWIS, J.L. WHITE and J.F. FELLERS, A.C.S., Polym. Prepr., 26(1), 255 (1985).

532. G. KISS. NRCC/IMRI symposium "Polyblends-'86", Montreal, Quebec, Canada, April 4, 1986; Polym. Eng. Sci., 27, 410 (1987).

533. N.M. REZANOVA and M.V. CEBRENKO, Kampoz. Polym. Materialy, 11, 47 (1981).

534. J.L. WHITE, A.P. PLOCHOCKI and H. TANAKA, Polym. Eng. Rev., 1, 217 (1981).

535. J.L. WHITE and K. MIN, in "Polymer Blends and Mixtures", I.J. Walsh, J.S. Higgins and A. Maconnachie, Eds., NATO ASI series E., Appl. Sci. No 89, pp. 413-28, Martinus Nijhoff Publ., Dordrecht (1985).

536. T. TAVGAC, PhD thesis, Univ. Houston (1972).

537. A.P. PLOCHOCKI, NRCC/IMRI symposium "Polyblends-'85", Boucherville, Que., Canada, April 16-17, 1985; Polym. Eng. Sci., 25, 82 (1985).

538. W. BERGER, H.W. KAMMER and C. KUMMERLÖWE, Makromol. Chem. Suppl., 8, 101 (1984).

539. J. MEISSNER, T. RAIBLE and S.E. STEPHENSON, J. Rheol., 25, 1 (1981).

540. N.P. KRASNIKOVA, V.E. DREVAL, E.V. KOTOVA and Z. PELZBAUER, Vysokomol. Soed., B23, 378 (1981).

541. V.E. DREVAL, G.V. VINOGRADOV, E.P. PLOTNIKOVA, M.P. ZABUGINA, N.P. KRASNIKOVA, E.V. KOTOCA and Z. PELZBAUER, Rheol. Acta, 22, 102 (1983).

542. N.P. KRASNIKOVA, E.V. KOTOVA, E.P. PLOTNIKOVA, M.P. ZABUGINA, G.V. VINOGRADOV, V.E. DREVAL, and Z. PELZBAUER, Kompoz. Polim. Mater., 21, 37 (1984).

543. S. WU, NRCC/IMRI symposium "Polyblends-'86", Montreal, Canada, April 4th 1986; Polym. Eng. Sci., 27, 335 (1987).

544. I. MILES, private communication (1986).

545. H. Van OENE, J. Colloid Interface Sci., 40, 448 (1972).

546. F.N. COGSWELL, Polym. Eng. Sci., 12, 69 (1972).

547. A.M. CATANI and L.A. UTRACKI, Proceed, Ann. Meet. Polymer Processing Society, Akron, OH, March 28-29, 1985; J. Polym. Eng., 6, 23 (1986).

548. A.P. PLOCHOCKI, in Vol 2 ref. [14].

549. A.P. PLOCHOCKI, Polym. Eng. Sci., 23, 618 (1983).

550. A.P. PLOCHOCKI, S.S. DAGLI and H. EMMANUILIDES, Amer. Chem. Soc., Polym. Prepr., 26, 288 (1985).

551. D.J. BYE and I.S. MILES, paper presented at 2nd Conf. Europ. Rheol., Prague, C.S.R (1986); Eur. Polym. J., 22, 185 (1986).

552. M.V. TSEBRENKO, A.V. YUDIN, T.I. ABLAZOVA and G.V. VINOGRADOV, Polymer, 17, 831 (1976).

553. M. RAPPAPORT, Plast. Eng., 41 (2), 33 (1985).

554. L.A. UTRACKI, Polym. Eng. Sci., 22, 1166 (1982).

555. P.J. PERRON, Adv. Polym. Technol., 6 (1), 79 (1986).

556. W. WITT, Materials and Design, 7 (4), 182 (1986).

557. A.J. KLEIN, Plastics Design Forum, May/June, 57 (1987).

558. L.M. ROBESON, Polym. Eng. Sci., 24, 587 (1984).

559. C.D. HAN, Y.W. KIM and S.J. CHEN, J. Appl. Polym. Sci., 19, 2831 (1975).

560. L.A. UTRACKI, Rheology and Processing of Multiphase Systems, Ch. 5.1 of "Current Topics in Polymer Science", R.M. Ottenbrite, L.A. Utracki and S. Inoue Eds., Hanser Publ., New York (1987).

561. S. WU, Polymer, 26, 1855 (1985).

562. H.K. ASAR, M.B. RHODES and R. SALOVEY, Adv. in Chem. Series, 176, 489-516 (1979).

563. J.R. STELL, D.R. PAUL and J.W. BARLOW, Polym. Eng. Sci., 16 (7), 496 (1976).

564. P.M. SUBRAMANIAN, Polym. Eng. Sci., 25 (8), 483 (1985).

565. P.M. SUBRAMANIAN, U.S. Pat. 4,410,482 (1983).

566. P.M. SUBRAMANIAN and M. MEHRA, Polym. Eng. Sci., 27, 663 (1987).

567. P.M. SUBRAMANIAN, Proceedings of Industrial Materials Research Institute Symposium "Polyblends-'87", Boucherville, Que., Canada, April 28-29, 9/1-9/21 (1987), submitted to Polym. Eng. Sci.

568. S.Y. HOBBS, J. Macromol., Sci.-Rev. Macromol. Chem., C19 (2), 221 (1980).

569. A. GARTON, Polym. Eng. Sci., 22, 124 (1982).

570. J.R. WHITE and E.L. THOMAS, Rubber Chem. and Technol., 57 (3), 457 (1984).

571. S. DANESI and R.S. PORTER, Polymer, 19, 448 (1978).

572. S.Y. HOBBS, J. Polym. Sci., Polym. Phys Edn., 16, 1321 (1978).

573. B.D. FAVIS and J.P. CHALIFOUX, Proceedings of Industrial Materials Research Institute Symposium "Polyblends-'87", Boucherville, Que., Canada, April 28-29, 12/1-12/35 (1987); submitted to Polym. Eng. Sci.

574. E. MASTUSCELLI, C. SILVESTRE, R. GRECO and C. RAGOSTA, Properties of Polystyrene - Polyolefin Alloys, in "Polymer Blends", E. Mastuscelli, R. Palumbo and M. Kryszewski, Eds., Plenum Press, New York (1980).

575. G.N. AVGEROPOULOS, F.C. WEISSERT, P.H. BIDDISON and G.C.A. BÖHM, Rubber Chem. and Technol., 49, 93 (1976).

576. L.P. MC MASTER, Adv. Chem. Ser., American Chemical Society, Washington, D.C., 142, 43 (1975).

577. J. KARGER-KOCSIS, A. KALLO and V.N. KULEZNEV, Polymer, 25, 279 (1984).

578. S.Y. HOBBS and V.H. WATKINS, J. Polym. Sci., Polym. Phys., Ed., 20, 651 (1982).

579. A. EINSTEIN, Ann. Physik, 19, 289 (1906).

580. G.I. TAYLOR, Proc. Royal Soc., A226, 34 (1954).

581. G.I. TAYLOR, Proc. Royal Soc., A146, 501 (1934).

582. G.I. TAYLOR, Proc. Royal Soc., A138, 41 (1932).

583. H.J. KARAM and J.C. BELLINGER, Ind. Eng. Chem., Fundam., 7, 576 (1968).

584. H.P. GRACE, Eng. Found. Res. Conf. Mixing, 3rd, Andover, N.H. (1974).

585. H.P. GRACE, Chem. Eng. Comm., 14, 225 (1982).

586. F.D. RUMSCHEIDT and S.G. MASON, J. Colloid Sci., 16, 238 (1961).

587. J.J. ELMENDORP, Polym. Eng. Sci., 26, 418 (1986).

588. J.J. ELMENDORP, and A.K. VAN DER VEGT, Polym. Eng. Sci., 26, 1332 (1986).

589. J.J. ELMENDORP, Ph.D. Thesis, Delft Univ. of Technology, The Netherlands (1986).

590. S. WU, Polym. Eng. Sci., 27, 335 (1987).

591. M.V. TSEBRENKO, N.M. REZANOVA and G.V. VINOGRADOV, Polym. Eng. Sci., 20, 1023 (1980).

592. L. D'ORAZIO, R. GRECO, C. MANCARELLA, E. MARTUSCELLI, G. RAGOSTA and C. SILVESTRE, Polym. Eng. Sci., 22, 536 (1982).

593. C. CIMMINO, L. D'ORAZIO, R. GRECO, G. MAGLIO, M. MALINCONICO, C. MANCARELLA, E. MARTUSCELLI, R. PALUMBO and C. RAGOSTA, Polym. Eng. Sci., 24, 48 (1984).

594. S. CIMMINO, F. COPPOLA, L. D'ORAZIO, R. GRECO, G. MAGLIO, M. MALINCONICO, C. MANCARELLA, E. MARTUSCELLI and G. RAGOSTA, Polymer, 27, 1874 (1986).

595. W.M. BARENTSEN, D. HEIKENS and P. PIET, Polymer, 15, 119 (1974).

596. W.M. BARENTSEN and D. HEIKENS, Polymer, 14, 579 (1973).

597. R.W. FLUMERFELT, Ind. Eng. Chem. Fundam., 11, (3), 312 (1972).

598. N. TOKITA, Rubber Chem. and Technol., 50, 292 (1977).

599. B.D. FAVIS, J.P. CHALIFOUX and P. VAN GHELUWE, 45th Annual Technical Conference, Society of Plastics Engineers Inc., (ANTEC), Los Angeles, May 4-7, 1987; S.P.E. Technical Papers, 33, 1343 (1987).

600. K. MIN, J.L. WHITE and J.F. FELLERS, J. Appl. Polym. Sci., 29, 2117 (1984).

601. J.L. WHITE and K. MIN, Advances in Polym. Technology, 5 (4), 225 (1985).

602. R.K. SENN, Mod. Plast. Encycl., 57, 362 (1980).

603. Farrel Co., Div. USM Corp., 25 Main St. Ansonia, CT.

604. P.R. VAN BUSKIRK, B. TURETZKY and B.F. GUNBERG, Rubber Chem. Technol., 48, 577 (1975).

605. E.S. DIZON and L.A. PAPAZIAN, Rubber Chem. and Technol., 50, 765 (1977).

606. G.E. O'CONNOR and J.B. PUTMAN, Rubber Chem. and Technol., 51, 799 (1978).

607. B.D. FAVIS and J.P. CHALIFOUX, Industrial Materials Research Institute Internal Report, Boucherville, Que., Canada (1987).

608. H.P. SCHREIBER and A. OLGUIN, Polym. Eng. Sci., 23, 129 (1983).

609. A.P. PLOCHOCKI, S.S. DAGLI, J. STARITA and J.E. CURRY, J. of Elastomers and Plastics, 18 (4), 256 (1986).

610. B.D. FAVIS and J.P. CHALIFOUX, Industrial Materials Research Institute Internal Report, Boucherville, Que., Canada (1987).

611. K. EISE, J. CURRY and J.F. NANGERONI, Polym. Eng. Sci., 23, 642 (1983).

612. T. BARTILLA, D. KIRCH, J. NORDMEIER, E. PRÖMPER and Th. STRAUCH, Advances in Polym. Technology, 6 (3), 339 (1986).

613. C.D. HAN, C.A. VILLAMIZAR and Y.M. KIM, J. Appl. Polym. Sci., 21, 353 (1977).

614. S. KOIWA, J. Appl. Polym. Sci., 19, 1625, (1975).

615. W.J. HO and R. SALOVEY, Polym. Eng. Sci., 21, 839 (1981).

616. P. CIELO, B.D. FAVIS and X. MALDAGUE, Proceedings of INRI Symposium "Polyblends-'87", Boucherville, Que., Canada, April 28-29, 13/1-13/36 (1987); submitted to Polym. Eng. Sci.

617. F.N. COGSWELL, B.P. GRIFFIN and J.B. ROSE, U.S. Pat. No. 4,438,236.

618. A. RUDIN and N.E. BRATHWAITE, Polym. Eng. Sci., 24, 1312 (1984).

619. E. NOLLEY, J.W. BARLOW and D.R. PAUL, Polym. Eng. Sci., 20, 364 (1980).

620. S.G. KIM and N.P. SUH, Polym. Eng. Sci., 26, 1200 (1986).

621. J.W. CURTIS, J. Phys. D., Appl. Phys., 3 (1970).

622. Z. TADMOR, J. Appl. Polym. Sci., 18, 1753 (1974).

623. J.L. WHITE and W. DIETZ, Polym. Eng. Sci., 19, 1081 (1979).

## LEGEND FOR FIGURES

Fig. 1 - Terminology

Fig. 2 - Free energy of mixing as a function of composition for a partially miscible system. The region of miscibility extends on both sides of the binodal composition $x_2'$ and $x_2''$. The inflection points (indicated by the arrows) indicate the spinodal compositions. Note that $\Delta\mu_i$ = constant within the immiscibility zone.

Fig. 3 - Lower (LCST) and upper (UCST) critical solution temperature: solid and broken lines indicate binodial and spinodial, respectively, $x_2$ is the mole fraction.

Fig. 4 - Schematic $\chi_{12}'$ vs T dependence indicating contributions from: 1. dispersion forces, 2. free volume, and 3. specific interactions. Solid lines - total effect in solvent/solvent or polymer/solvent (a) and polymer/polymer (b) systems. The dotted line $\chi'$ indicates critical value of $\chi_{12}$. After Patterson and Robard [27].

Fig. 5 - Schematic dependence of the overall interaction parameter $\chi_{12}'$ on copolymer composition, $\phi_A$, and copolymer interaction parameter $\chi'$ (after [45]).

Fig. 6 - Comparison of $q_m$ vs $\tau$ behavior found in small molecule systems (A), inorganic glasses (B), metallic alloys (C) and high molecular weight polymer blends (points). Also shown is a fit to Equation (18) (D) [52].

Fig. 7 - Computer simulated concentration distribution during spinodal decomposition, in critical and off-critical quench. The degree of darkness is proportional to the local concentration [56].

Fig. 8 - Melting temperatures in LDPE/EPDM blends. Data from [94], curves Eq (20).

Fig. 9 - SAXS for SB with 30 wt% PS. B and S indicate position of binodal and spinodal temperature, respectively. Data [116].

Fig. 10 - Concentration dependence of the interaction parameter $\chi_{23}$ at 182 and 200°C for cellulose acetate/polyacetal blends [173, 174].

Fig. 11 - $T_g$ - composition dependence as predicted by Eq (28) for the indicated values of k. $T_{g1}$ = 300 and $T_{g2}$ = 500 K were assumed. Note that linearity requires that k = 1.20925.

Fig. 12 - Glass transition temperature vs poly(2,6-dimethyl-1,4-phenylene oxide) content for its blends with: (1) poly-(4-chlorostyrene), (2) poly(styrene-r-4-chlorostyrene) containing 68.6 mol % of 4-chloro styrene; (3) as in (2) but 58.5 mol % of 4-chloro styrene. Data from Ref. [189]. (---)No measurements available.

Fig. 13 - $T_g$ of ABS blends vs weight percent of the second component: (1) Poly(styrene-co-methylacrylate-co-methylmethacrylate), (2) Polycarbonate. Lines Eq (28); points experimental [190].

Fig. 14 - $T_g$ vs weight fraction of PVC in its blends with NBR. Curves Eq

(28) with k = 2/3, K* = 1.5; points experimental [191].

Fig. 15 - The concentration dependence $T_g$ for poly(β-hydroxyethyl - 3,5 dinitrobenzoyl methacrylate) blend with poly(N- methyl-3-hydroxy carbazolyl methacrylate), top, and with poly(N-ethyl-3-hydroxy carbazolyl methacrylate). Curves Eq (31); points experimental [193].

Fig. 16 - Relative viscosity for monodispersed hard sphere suspensions. Points experimental [422]; curves-theoretical with $[\eta]_s$ = 2.5: solid line, Eq (51) with $\phi_m$ = 0.78, broken line, Eq (52) with $\phi_m$ = 0.91.

Fig. 17 - Correlation between $\Delta G_m$ and logη plotted vs weight fraction of POM for its blends with cellulose acetate/butyrate, CAB [492].

Fig. 18 - Correlation between the maximum value (ordinate) of the reduced frequency relaxation spectrum, $\tilde{H}_{G,max}$, and molecular weight ratio, $M_n/M_w$ for miscible (solid line) and immiscible (broken line) LLDPE blends [43].

Fig. 19 - Cole-Cole plot for three systems: (1) PC - solid line, adjusted to coincide with high frequency data of system (2) PC with 24 wt% of TMPC and 4% PS (solid points), and (3) PC with 35 wt% PS (open points) [506, 507].

Fig. 20 - Isochronal G' (at $\omega = 10^{-2}$ and $10^{2}$ rad/s) vs weight fraction of the second component for linear low density polyethylene, LLDPE, blended

with another LLDPE or with low density polyethylene, LDPE [43].

Fig. 21 - G' of linear low density polyethylene, LLDPE, blends with another LLDPE or with low density polyethylene, LDPE. The data taken at 190°C and constant G" = $10^2$ (bottom) and $10^4$ Pa. The same data as shown in Fig. 18 [43].

Fig. 22 - Steady state extensional viscosity of blends of two different linear low density polyethylenes as a function of composition. Points - experimental, curve - second order polynomial [515].

Fig. 23 - Shear viscosity ratio of polyethylene, PE (minor phase, 30%) and polystyrene, PS, vs shear stress, $\sigma_{12}$, at 180°C for six PE/PS blends. Lines indicated $\sigma_c$ and MF represent the limiting values for droplet formation and melt fracture, respectively. Data from capillary and rotational shear [540].

Fig. 24 - Notched Izod impact strength for rubber/nylon blends versus number average particle diameter, $d_n$, at constant adhesion $G_a$ = 8100$Jm^{-2}$. Rubber contents, curve I: 10%; curve II: 15%; curve III: 25% by weight. Solid symbols are for tough fracture; open symbols are for brittle fracture [561].

Fig. 25 - Notched impact toughness versus (surface to surface) imterparticle distance, showing that the tough-brittle transition occurs at a critical value independent of rubber volume fraction. Rubber contents: curve I: 25%; curve II: 15%; curve III: 10% [561].

Fig. 26 - Hydrocarbon permeability in laminar walled high density polyethylene/nylon barrier bottles. Curve I represents permeability in HDPE; curve II represents HDPE + 20% nylon; curve III represents HDPE + modified laminar nylon [564].

Fig. 27 - Scanning electron micrographs of polypropylene in nylon illustrating: a) ploughing; b) absence of ploughing. Photographs taken by Dr. J. Willis, Industrial Materials Research Institute.

Fig. 28 - Critical value of droplet deformation, $E_c$, versus viscosity ratio, $\lambda$, for droplet breakup in uniform shearing flow [536]: O data due to Tavgac [536]; O data due to Taylor [581]; - - - curve drawn through the data obtained by Karam & Bellinger [583].

Fig. 29 - Effect of the viscosity ratio, $\lambda$, on the critical value of droplet deformation, $E_c$, in a hyperbolic flow field, with various values of medium viscosity (N sec/$m^2$) [584]: O 1.1; O 4.55.

Fig. 30 - Schematic showing modes of droplet deformation in different flow fields at various viscosity ratios [586]. Hyperbolic flow field a) viscosity ratio, $\lambda = 2 \times 10^{-4}$; b) $\lambda = 1.0$. Shear flow field a) $\lambda = 2 \times 10^{-4}$; b) $\lambda = 1.0$; c) $\lambda = 0.7$; d) $\lambda = 6.0$.

Fig. 31 - The change in morphology as a function of torque ratio and composition for blends of ethylene propylene diene terpolymer (EPDM) and polybutadiene (BR) [575].

Fig. 32 - The dependence of phase size on torque ratio for polypropylene/

polycarbonate blends [573].

Fig. 33 - The effect of torque ratio on the phase size/composition dependence for blends of polypropylene (PP) and polycarbonate (PC). PP-1 is a low viscosity polypropylene; PP-2 is a high viscosity polypropylene [599].

**Table 1. Polyblends Terminology**

| | |
|---|---|
| **POLYMER BLENDS (PB):** | **Mixtures of polymers and/or copolymers.** |
| **POLYMER ALLOYS (PA):** | **Immiscible, compatibilized polymer blends with modified interfacial properties and/or morphology.** |
| MISCIBLE PB: | PB behaving as a single-phase system down to segmental level of dispersion, usually associated with $\Delta H_m < 0$. |
| COMPATIBLE PB: | Utilitarian term indicating commercially attractive PB; usually homogeneous to-the-eye with enhanced physical properties. |
| COMPATIBILIZATION: | Any physical or chemical action which results in stabilization (prevention to separate) of PB morphology and properties. |
| ENGINEERING POLYMER (EP): | Processable polymeric material, capable of being formed to precise and stable dimensions, exhibiting high mechanical properties at continuous use temperature T 100°C |
| ENGINEERING PB (EPB) : | PA or PB exhibiting properties and/or containing EP as at least one component of the blend. |

Table 2. Historical Brief on Development of Polymer Alloys and Blends

| NO. | YEAR | EVENT | REFERENCE |
|---|---|---|---|
| 1. | 1846 | First patenting of polymer blend: natural rubber with gutta percha | T. Hancock, Engl. Pat. No. 11,147 |
| 2. | 1942 | First patent on thermoplastic polymer blends: polyvinyl chloride, PVC, with NBR as a permanent semi-soluble polymeric plasticizer. (Plasticization of PVC was invented 16 years earlier). | E. Badum, U.S. Pat. No. 2,297,194 (1942); D.E. Henderson, U.S. Pat. No. 2,330,353 (1943) to B.F. Goodrich Co. W.L. Semon, U.S. Pat. No. 1,929,453 of October 1933. |
| 3. | 1942 | First use of the term "alloy" in reference to thermoplastics:"Styralloy-22" commercialized by Dow Chem. Co. interpenetrating polymer network,IPN, of styrene and butadiene. | R.F. Boyer, in "History of Polymer Science and Technology, R.B. Seymour, Ed., M. Dekker, New York (1982). |
| 4. | 1960 | Discovery of miscibility of PS with polyphenylene ethers PPE invented in the late 50's by A.S. Hay, (JACS, 81, 6335 (1959)) led to a whole family of Noryl blends commercialized in 1965. | E.M. Boldebuck, U.S. Pat. No. 3,063,851 (1962); E.P. Cizek, U.S. Pat. No. 3,383,4435 (1968) to General Electric Co. |
| 5. | 1975 | Development at DuPont of "super tough nylon", Zytel-ST, followed by toughening of polyethyleneterephthalate, PET, by addition of small quantity of polyolefinic elastomer. | "Nylon ST super tough Nylon Resin" bulletin E29250 by DuPont. |
| 6. | 1977 | Mobay starts production of Bayblend containing polycarbonate, PC, and ABS on licence from Borg Warner who simultaneously introduced ABS/PC blend under the trade name Cycoloy. | J.J. Gasparich, "CANPLAST-'81", Montreal, Que., Canada, Oct. 25, 1981. |
| 7. | 1983 | Noryl GTX, blend of PPE with polyamide, PA, starts a new family of high performance GEC blends, Noryl Plus. | Chem. Weeks, Nov. 27, 1985, p. 108. |
| 8. | 1983 | ATOCHEM introduces two blends based on its proprietary polyetherblockamide, PEBA: Orgater = PBT/EVA/PEBA and Rilsan PA/PEBA (powder coating). | J.-L. Arraou, Caoutch. Plast., Juin-Juil., 1986, p. 79. |
| 9. | 1986 | New blends for car interior, Pulse, PC/ABS type, developed by Dow Chem. Co. | Plast. Technolog., April 1986, p. 103. |

**Table 3. Example of Miscible Polymer Pairs [41, 42].**

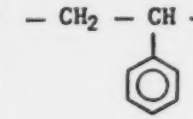
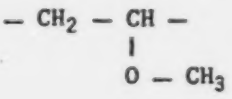
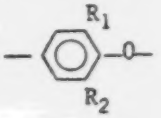
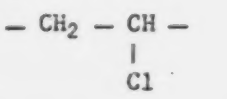
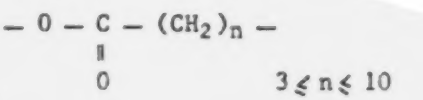
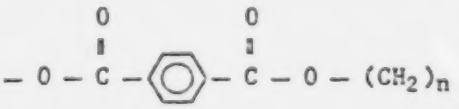
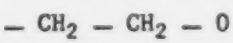
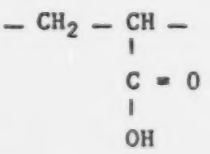
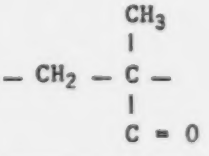
| No. | Polymer 1 | No. | Polymer 2 |
|---|---|---|---|
| I | Polystyrene, PS<br>  | 1. | Polyvinylmethylether, PVME<br>  |
| | | 2. | Poly(2,6 di-alkyl phenylene ethers), PPE<br>$R_1 = -CH_3, -C_2H_5, -C_3H_7$<br>  |
| II | Polyvinylchloride, PVC<br>  | 1. | Polyesters<br>  |
| | | 2. | Polybutyleneterephthalate, PBT<br>  |
| III | Polyethyleneoxide, PEO<br>  | 1. | Polyacrylic acid, PAA<br>  |
| | | 2. | Polymethacrylic acid, PMA<br>  |

**Table 3. (cont.)**

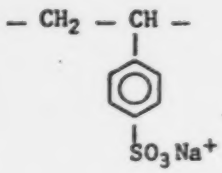
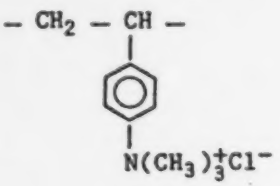
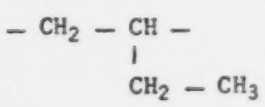
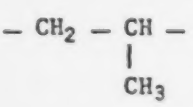
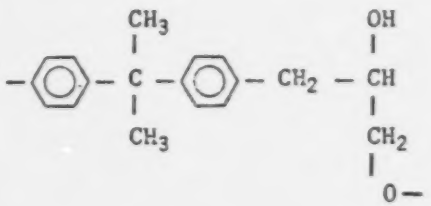
| No. | Polymer 1 | No. | Polymer 2 |
|---|---|---|---|
| IV | Poly(sodium styrene sulfonate)<br>  | 1. | Poly(vinylbenzyltrimethyl amonium chloride)<br>  |
| V | Polybutylene-1, PB<br>  | 1. | Polypropylene, PP<br>  |
| VI | Phenoxy<br>  | 1.<br>2. | PVME<br>PEO |
| VII | PVC | 1. | Poly(butadiene-co-acrylonitryle) with 30 to 40% acrylonitryle content. |
| | | 2. | poly(ethylene-co-vinyl acetate) with 60 to 75% vinyl acetate content. |

**Table 4. Determination of Polymer Blend Miscibility (see text)**

| No. | Method | Comments |
|---|---|---|
| I.1 | Melting point depression | assumes $\chi'_{12}$ = const. |
| I.2 | Analog calorimetry | assumes $\chi'_{12} = \chi'_{12_h}$ = const. |
| I.3 | Turbidimetry/Scattering | can give: phase diagram, $\chi'_{12}$, coil dimension,... |
| I.4 | Fluorescence | requires chromofor and calibration |
| I.5 | Hess cycle | assumes $\chi'_{12}$ = const. |
| I.6 | Inverse gas chromatography | $\chi'$-value probe-specific |
| I.7 | Gel permeation chromatography | allows determination of phase diagram |
| II.1 | Glass transition temperature | miscibility concluded from $T_g$ vs composition and from peak broadening |
| II.2 | Spectroscopy | gives information on source and magnitude of specific interactions |
| II.3 | Microscopy | qualitative |
| II.4 | Rheology | allows determination of miscibility in solid as well as molten state |

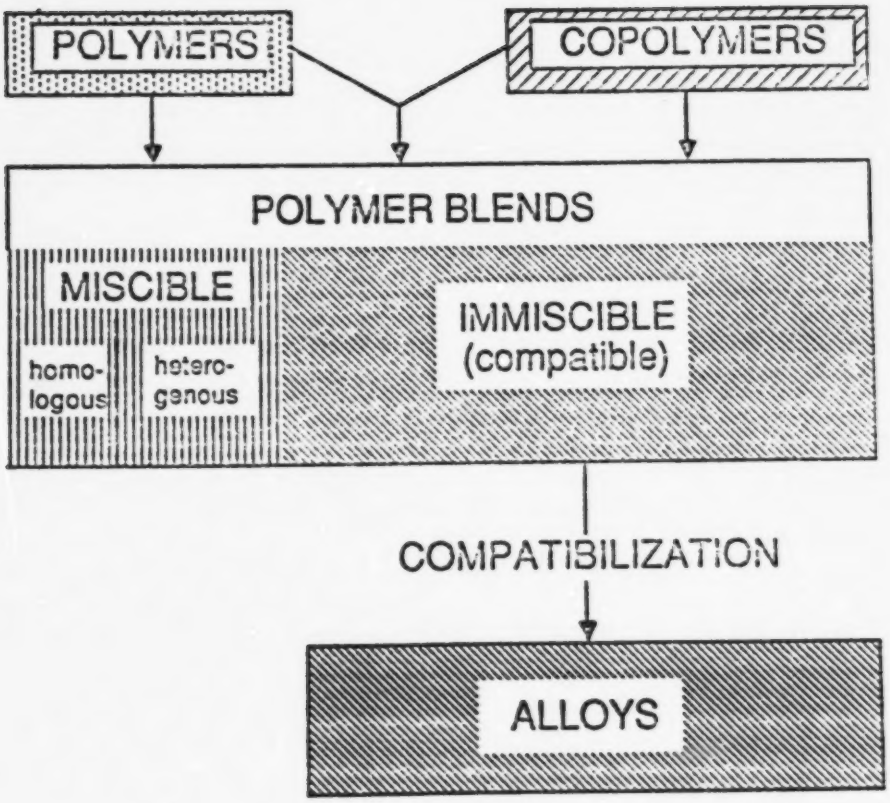
**Table 5 Fluorescence Techniques [158]**

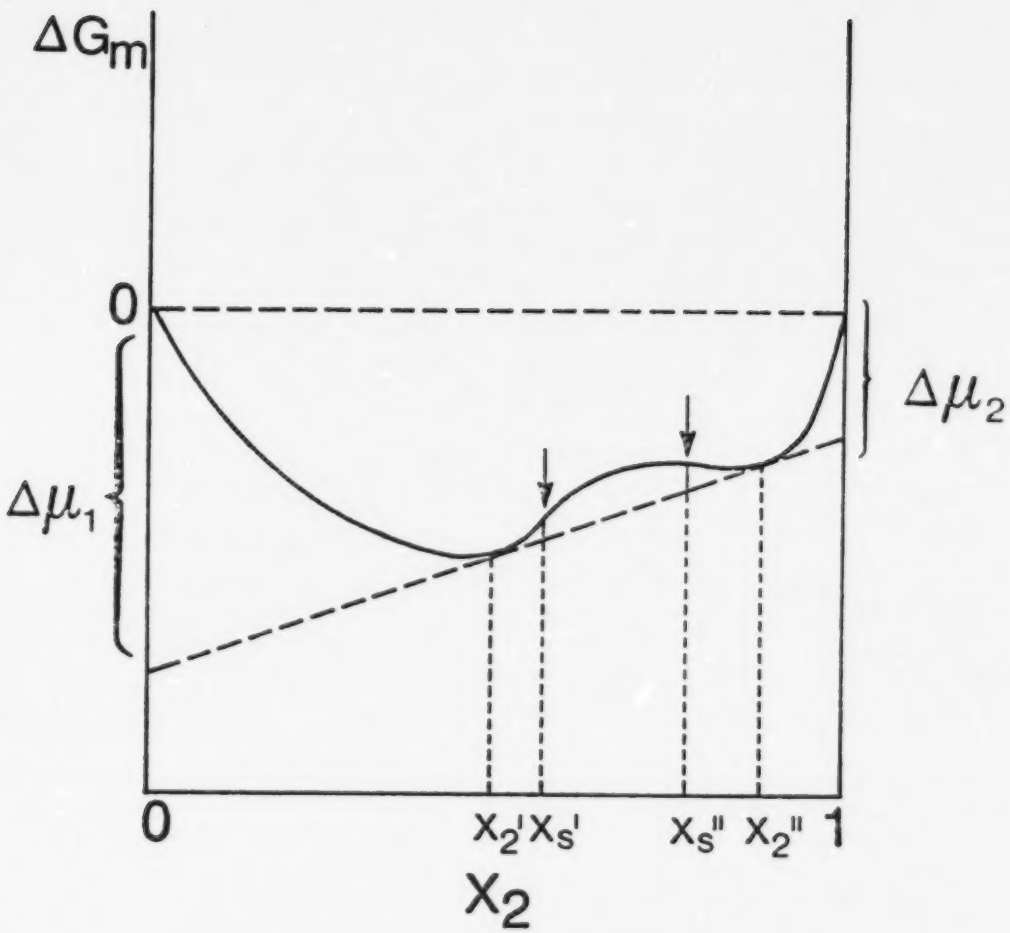
| A. TECHNIQUES | | |
|---|---|---|
| steady state measurements | transient techniques | time scale |
| fluorescence spectra | fluorescence decay | nanoseconds |
| phosphorescence spectra | phosphorescence decay | nanoseconds to seconds |
| polarization | polarization decay | nanoseconds to seconds |
| **B. PROCESSES** | | |
| reaction | observation | spatial scale (nm) |
| energy transfer<br>$A^* + B \rightarrow B^* + A$ | emission from B | 1 to 8 |
| excimer and exciplex formation<br>$A^* + A \rightarrow (AA)^*$<br>$A^* + D \rightarrow (AD)^*$ | new emission from (AA)* or (AD)* | 0.5 |
| quenching, self-quenching<br>$A^* + Q \rightarrow A + Q$<br>$A^* + A \rightarrow 2A$ | decreased emission intensity; shorter decay time | 0.5 to 1.5 |

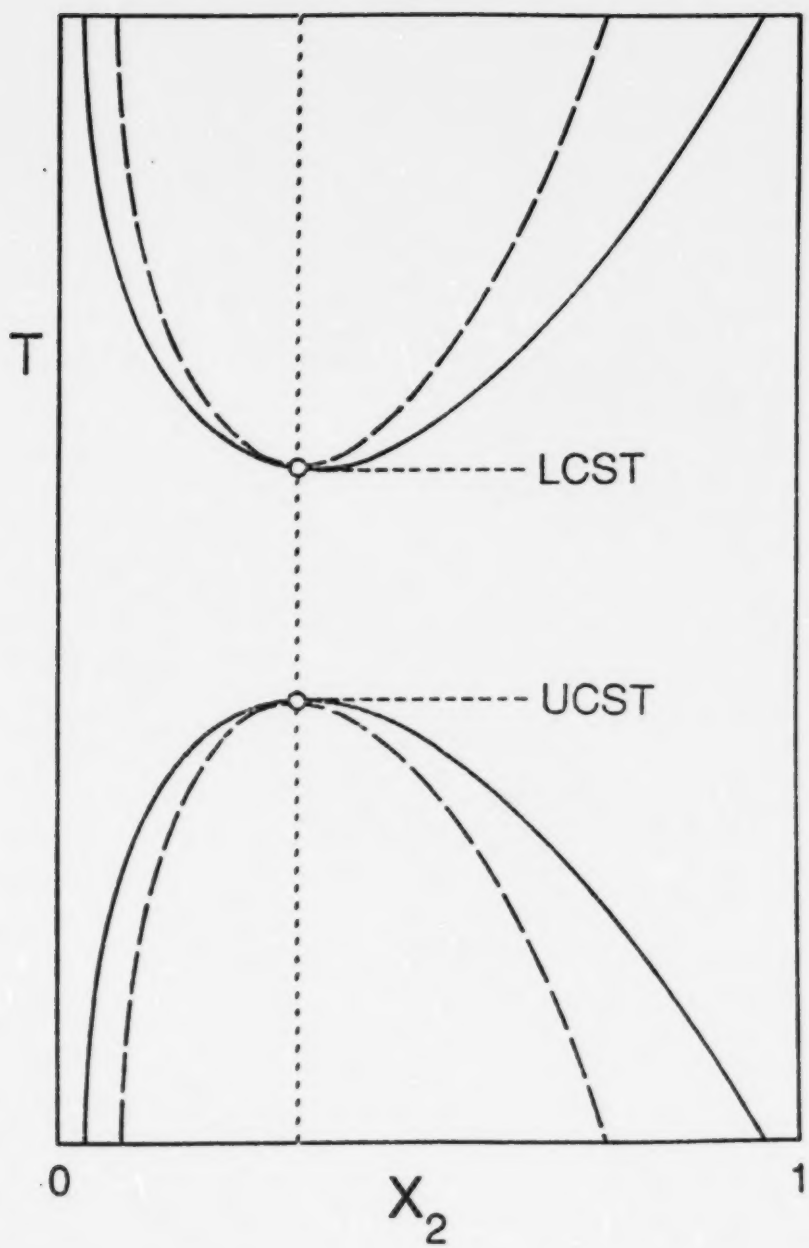
**Table 6. Aspect ratio dependence of [n] and $1/\phi_m$ (Eq 53).**

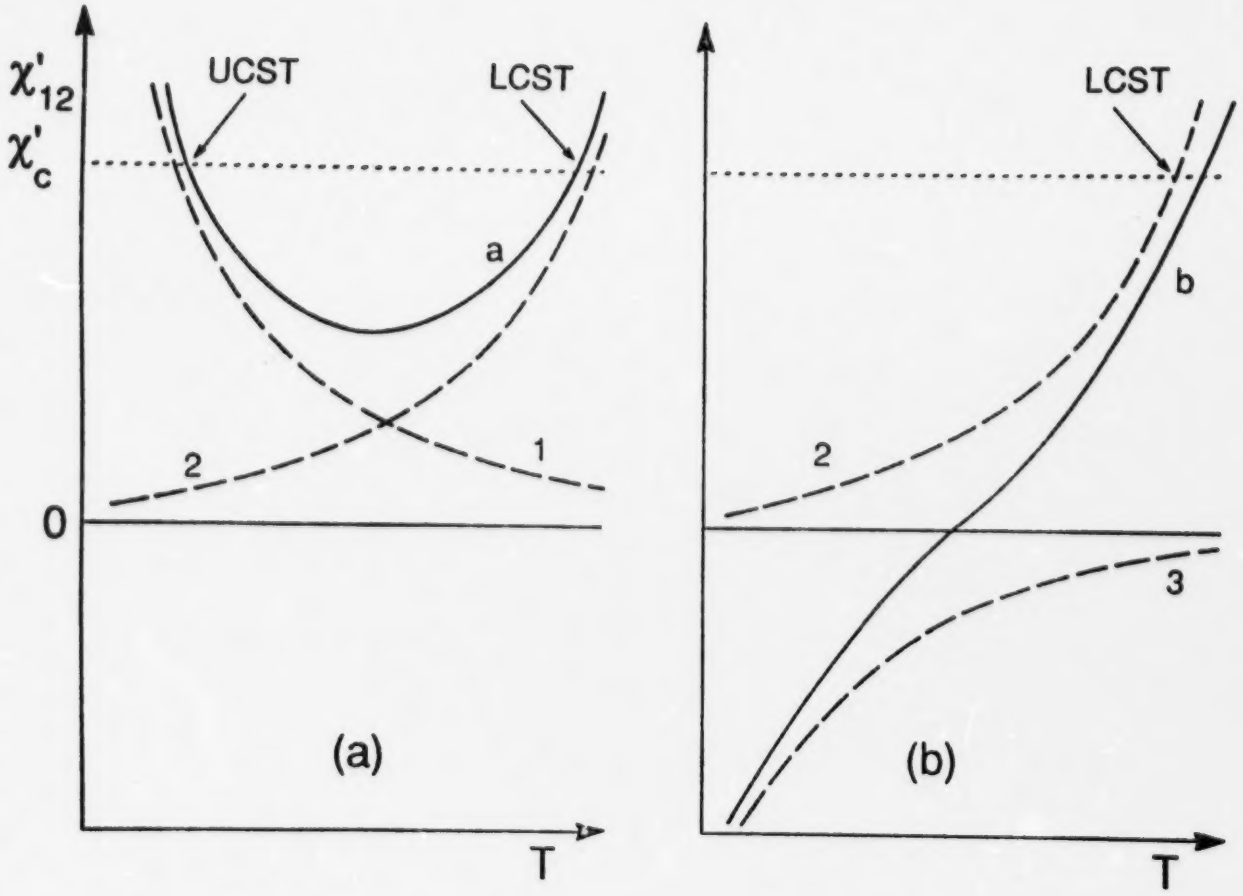
| No | Particle Shape | Y | $p_m$ | $a_0$ | $a_1$ | $a_2$ | Reference |
|---|---|---|---|---|---|---|---|
| 1 | Discs | [n] | 50 | 2.51 | 0.1127 | 1 | 423 |
| 2 | Discs | $1/\phi_m$ | 50 | 1.29 | 0.0598 | 1 | 375 |
| 3 | Rods | [n] | 50 | 2.34 | 0.1636 | 1 | 375 |
| 4 | Rods | $1/\phi_m$ | 150 | 1.38 | 0.0376 | 1.4 | 424 |

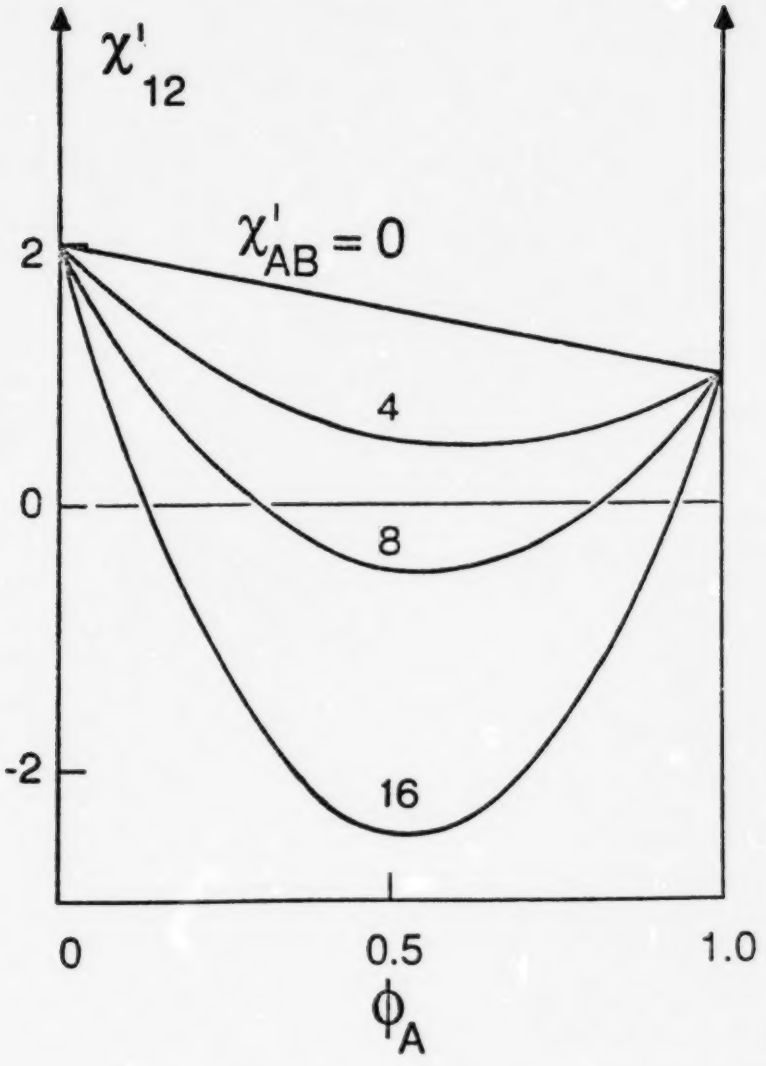
Note: $p_m$ indicates the maximum value of the aspect ratio used to determine the parameters $a_i$.

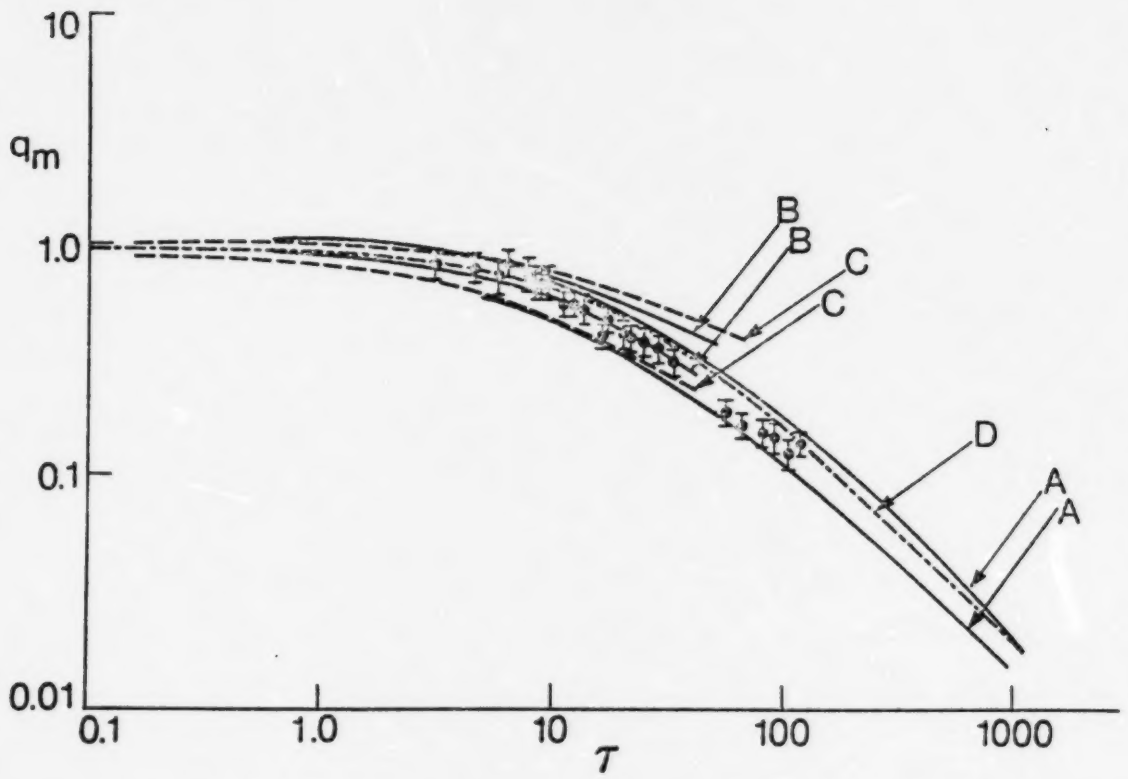

POLYMERS
COPOLYMERS
POLYMER BLENDS
MISCIBLE
homo-
logous
hetero-
genous
IMMISCIBLE
(compatible)
COMPATIBILIZATION
ALLOYS

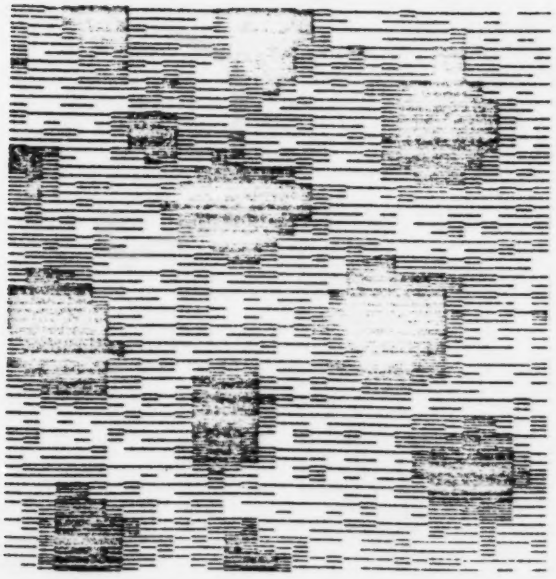

ΔGm
0
Δμ1
Δμ2
0
x2' xs'
xs'' x2''
1
X2

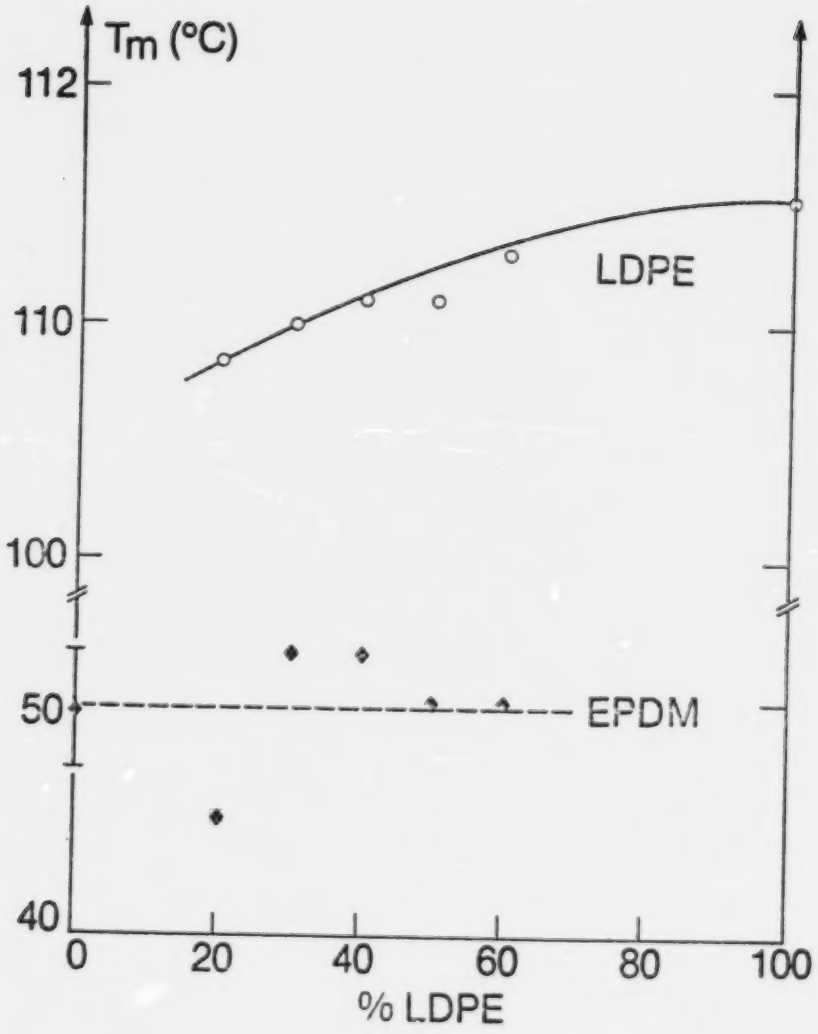

T
LCST
UCST
0
1
$X_2$

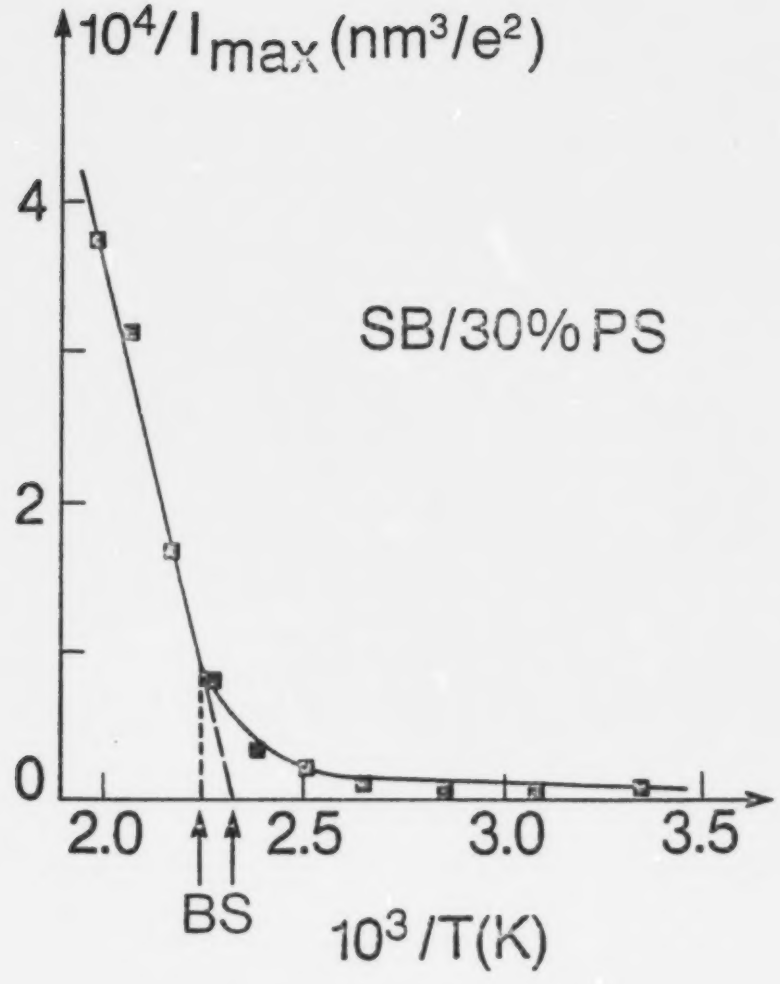

$\chi'_{12}$
$\chi'_c$
UCST
LCST
a
1
2
0
(a)
T
LCST
b
2
3
(b)
T

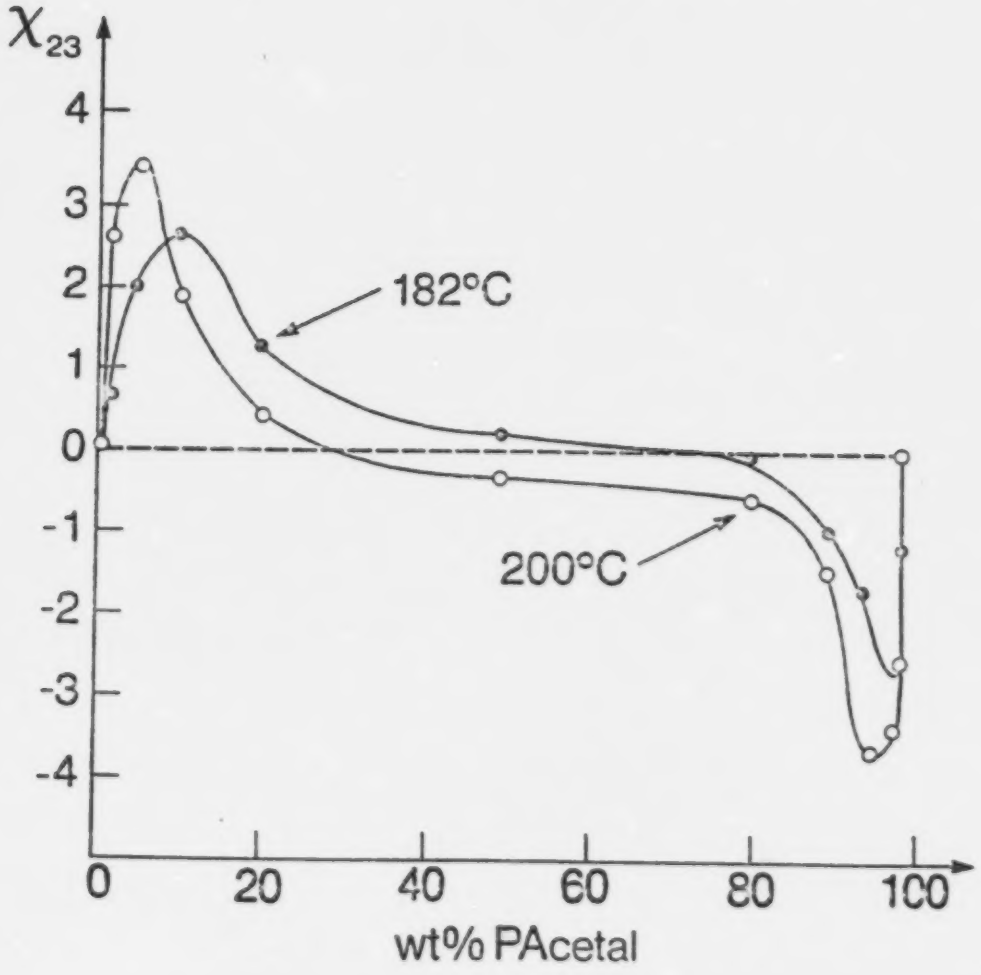

$\chi'_{12}$
$\chi'_{AB} = 0$
2
4
0
8
-2
16
0
0.5
1.0
$\phi_A$

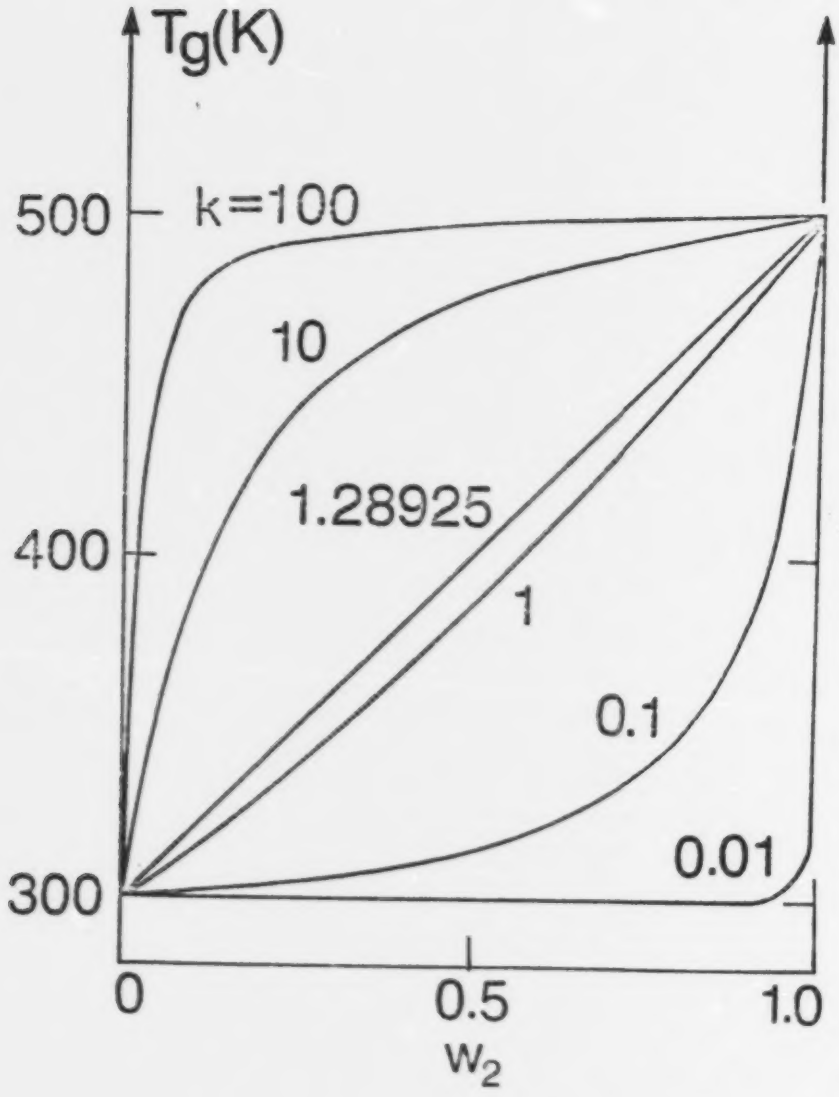

10
$q_m$
1.0
0.1
0.01
0.1
1.0
10
100
1000
$\tau$
B
B
C
C
D
A
A

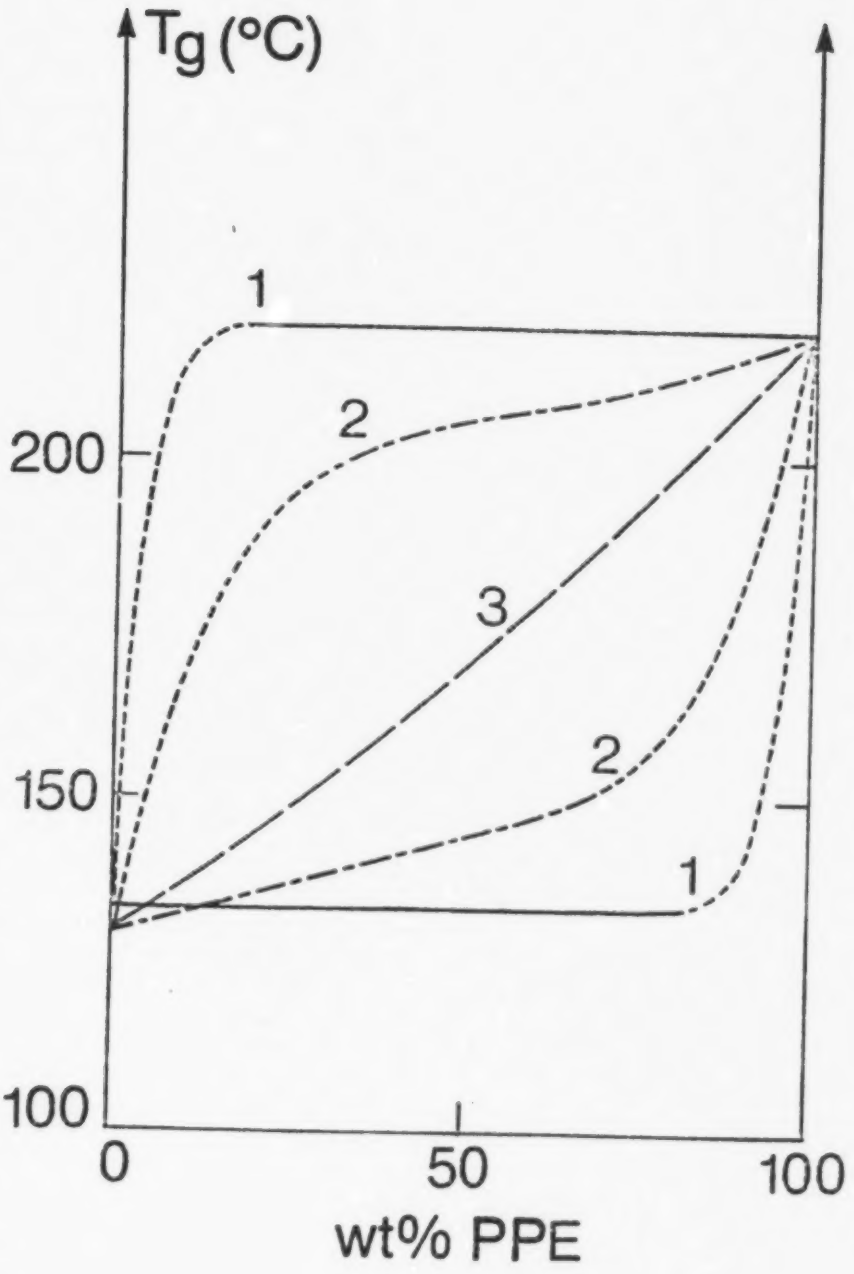


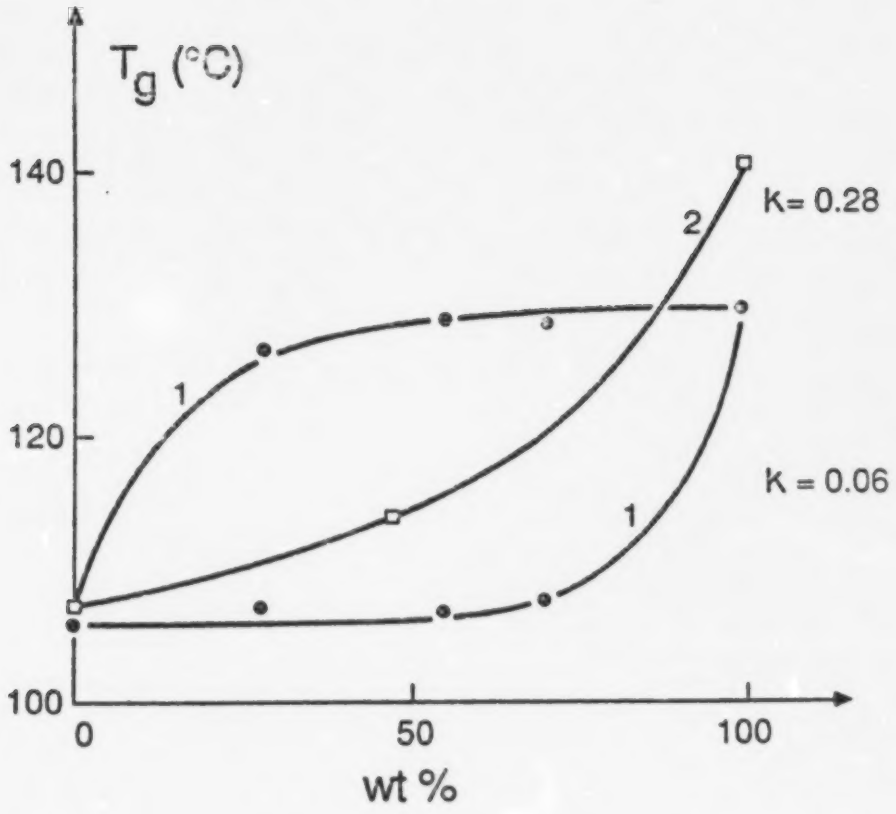

Tm (°C)
112
110
100
50
40
LDPE
EPDM
0
20
40
60
80
100
% LDPE

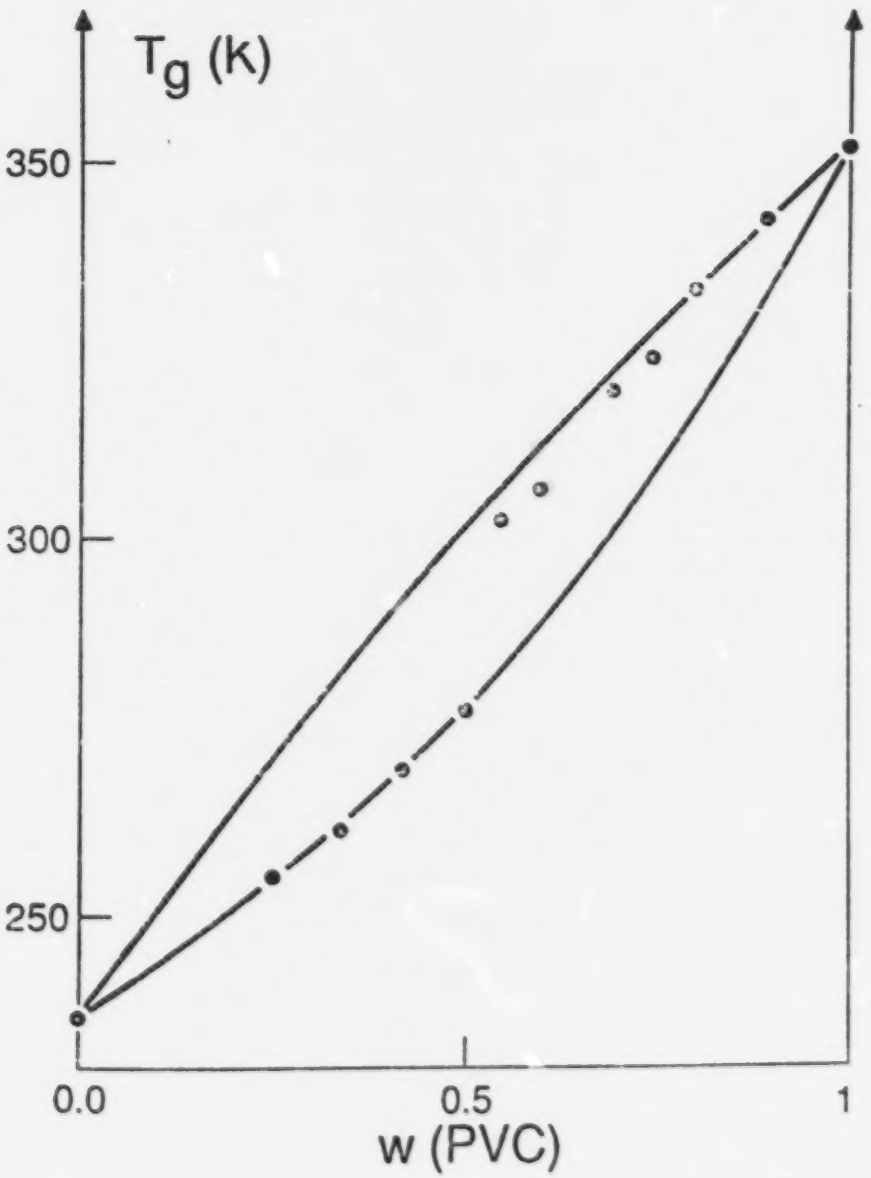

$10^4/I_{max}\,(nm^3/e^2)$
4
2
0
SB/30% PS
2.0
2.5
3.0
3.5
BS
$10^3/T(K)$

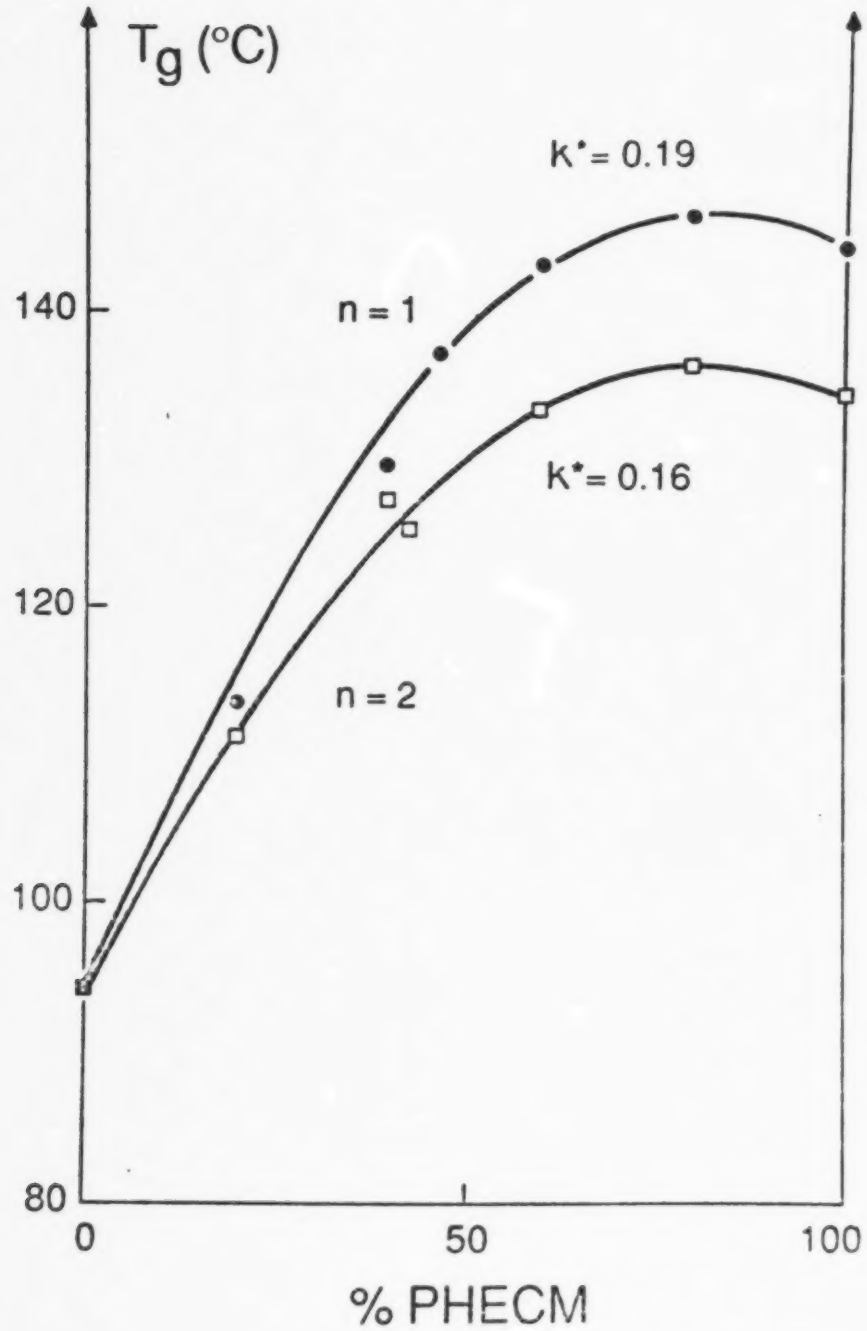

$\chi_{23}$
4
3
2
1
0
-1
-2
-3
-4
182°C
200°C
0
20
40
60
80
100
wt% PAcetal

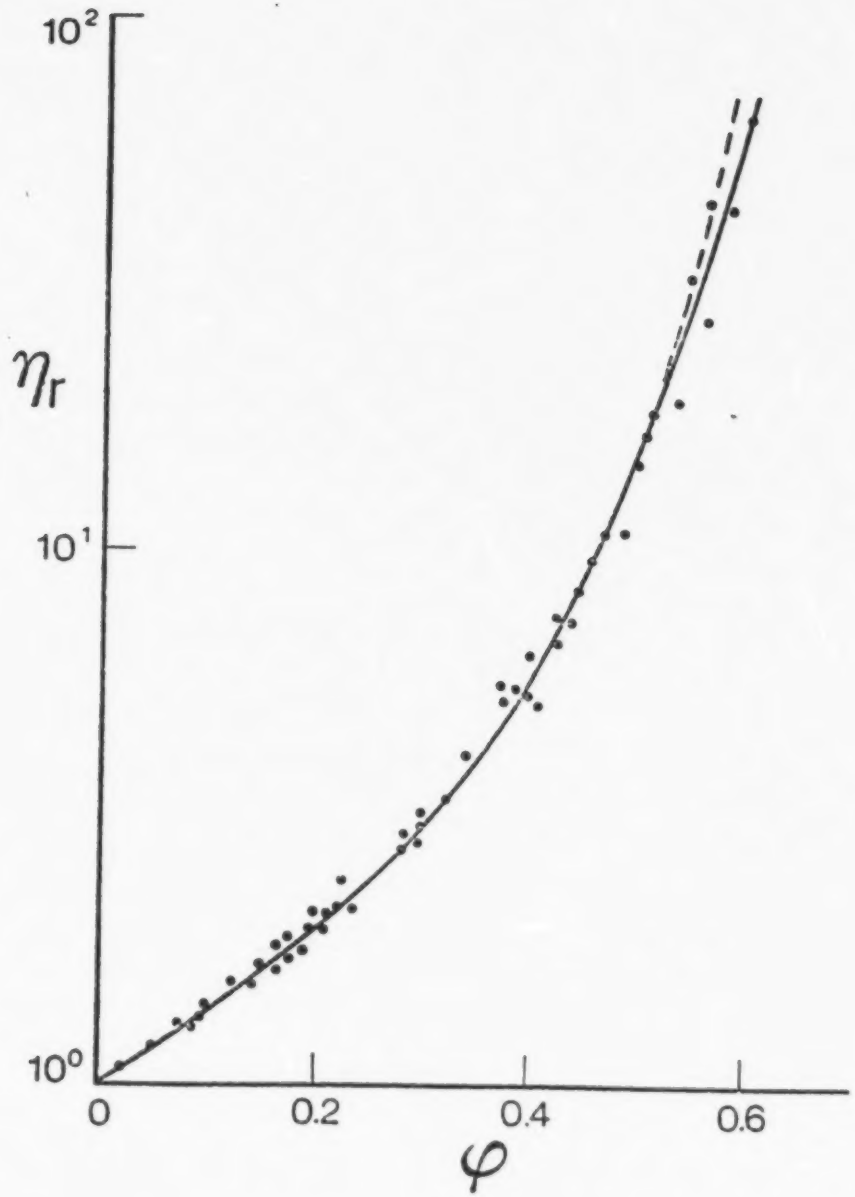

Tg(K)
500
400
300
k=100
10
1.28925
1
0.1
0.01
0
0.5
1.0
w2


Tg (°C)
200
150
100
1
2
3
2
1
0
50
100
wt% PPE


$T_g$ (°C)
140
120
100
0
50
100
wt %
1
2
1
k= 0.28
k = 0.06


$T_g$ (K)
350
300
250
0.0
0.5
1
w (PVC)


$T_g$ (°C)
K* = 0.19
n = 1
K* = 0.16
n = 2
140
120
100
80
0
50
100
% PHECM


$10^2$
$\eta_r$
$10^1$
$10^0$
0
0.2
0.4
0.6
$\varphi$

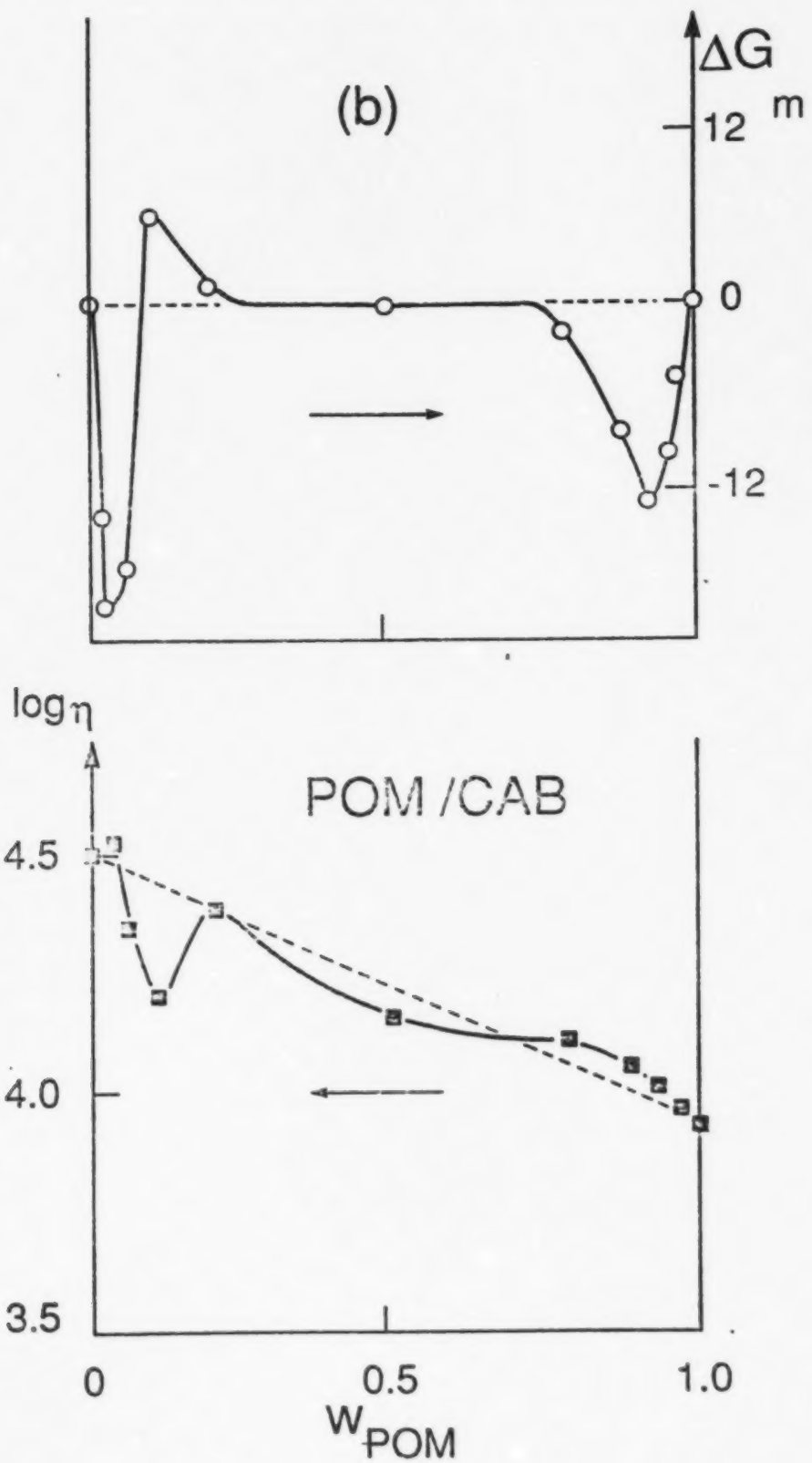
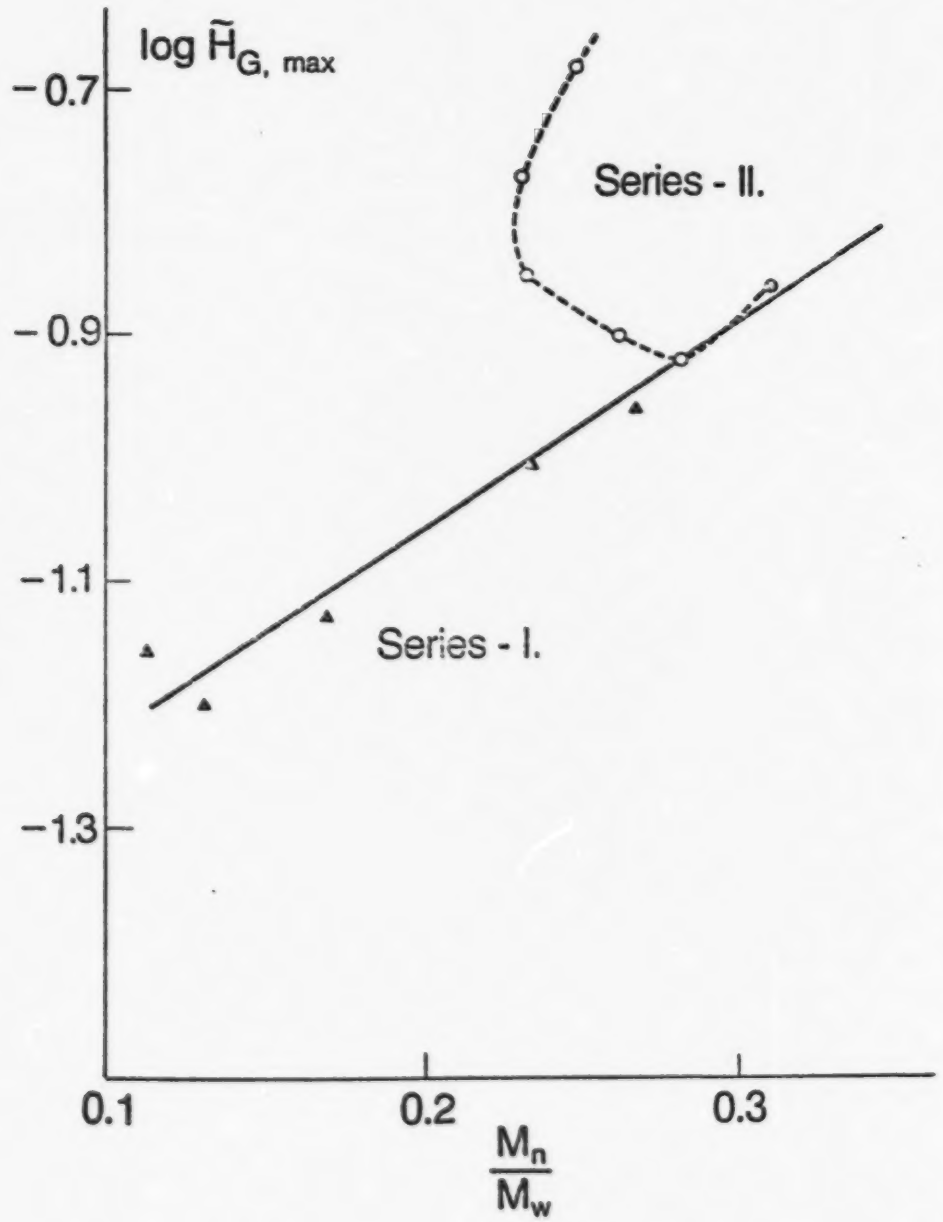
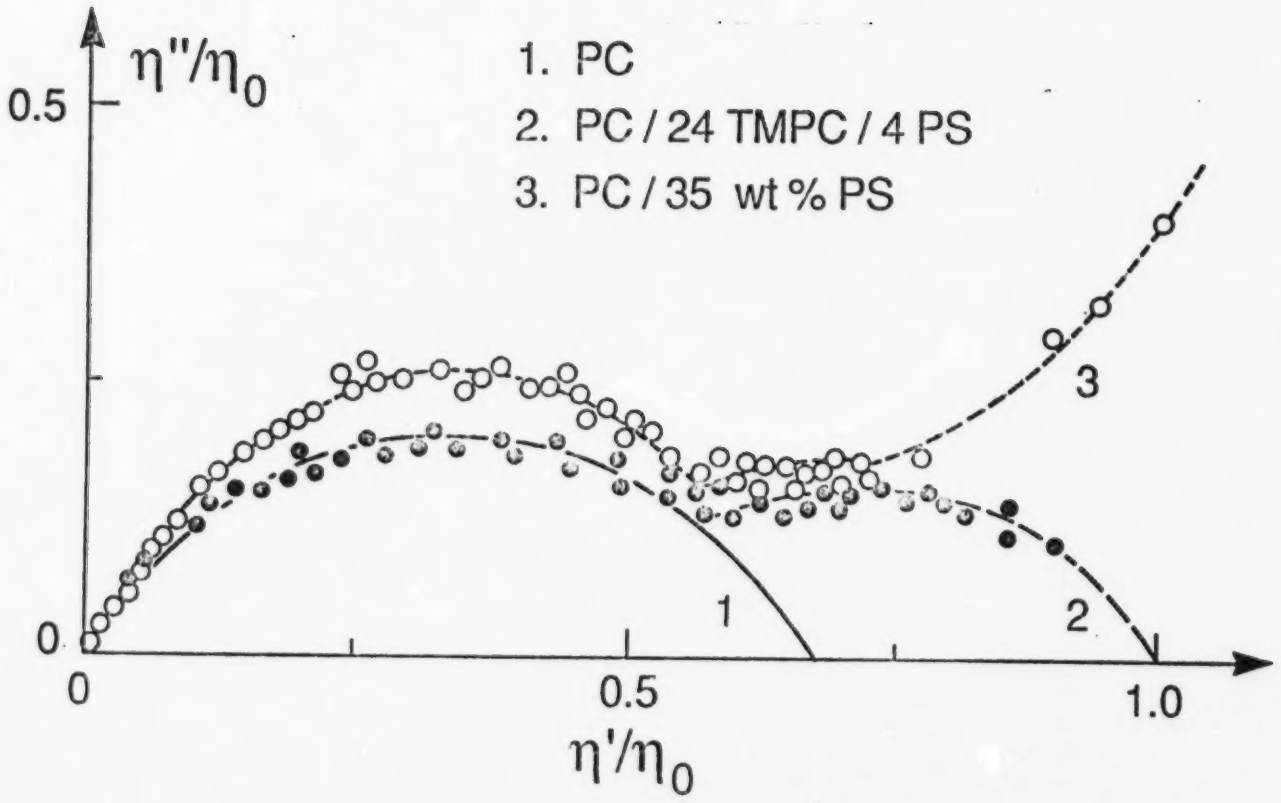
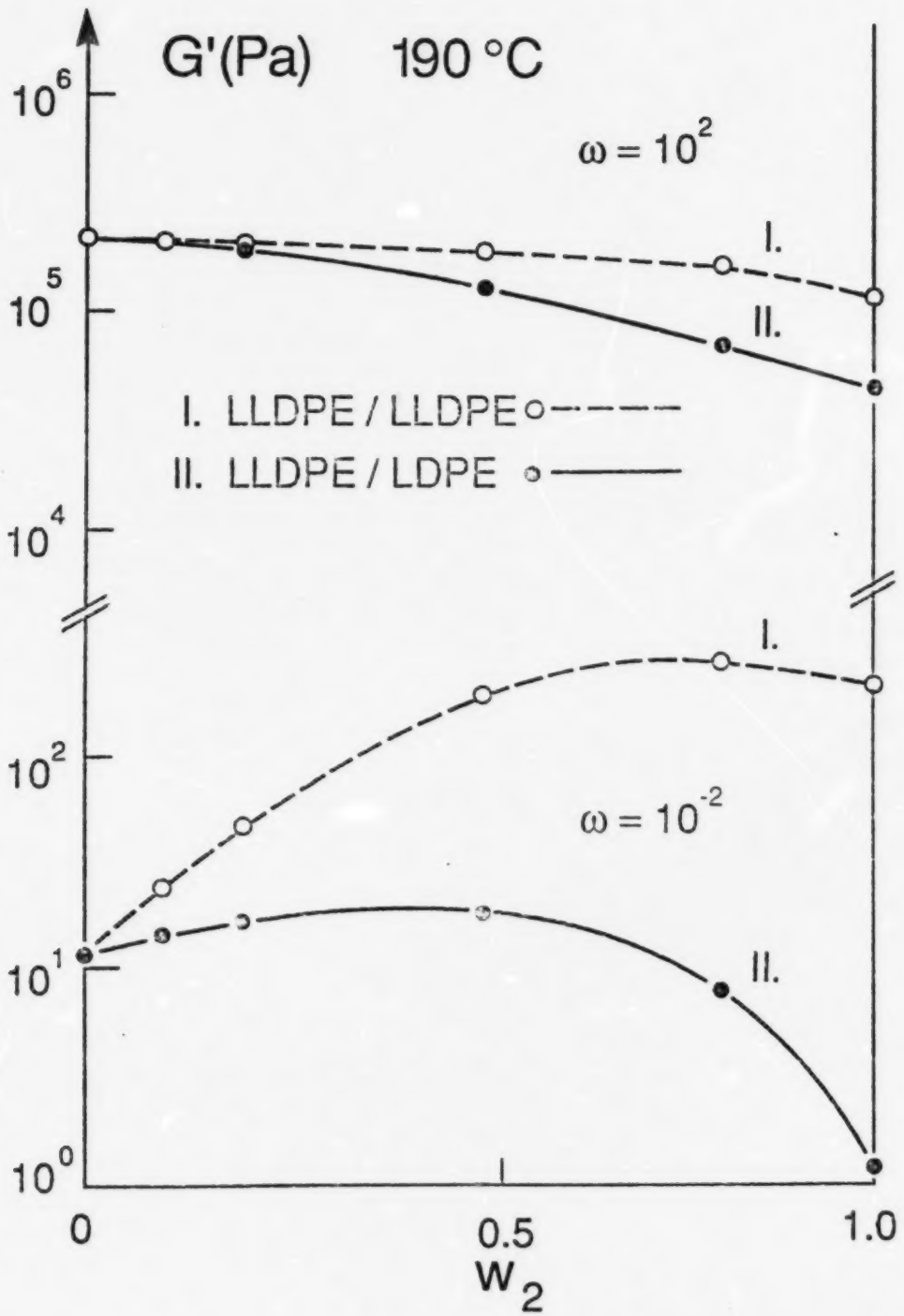
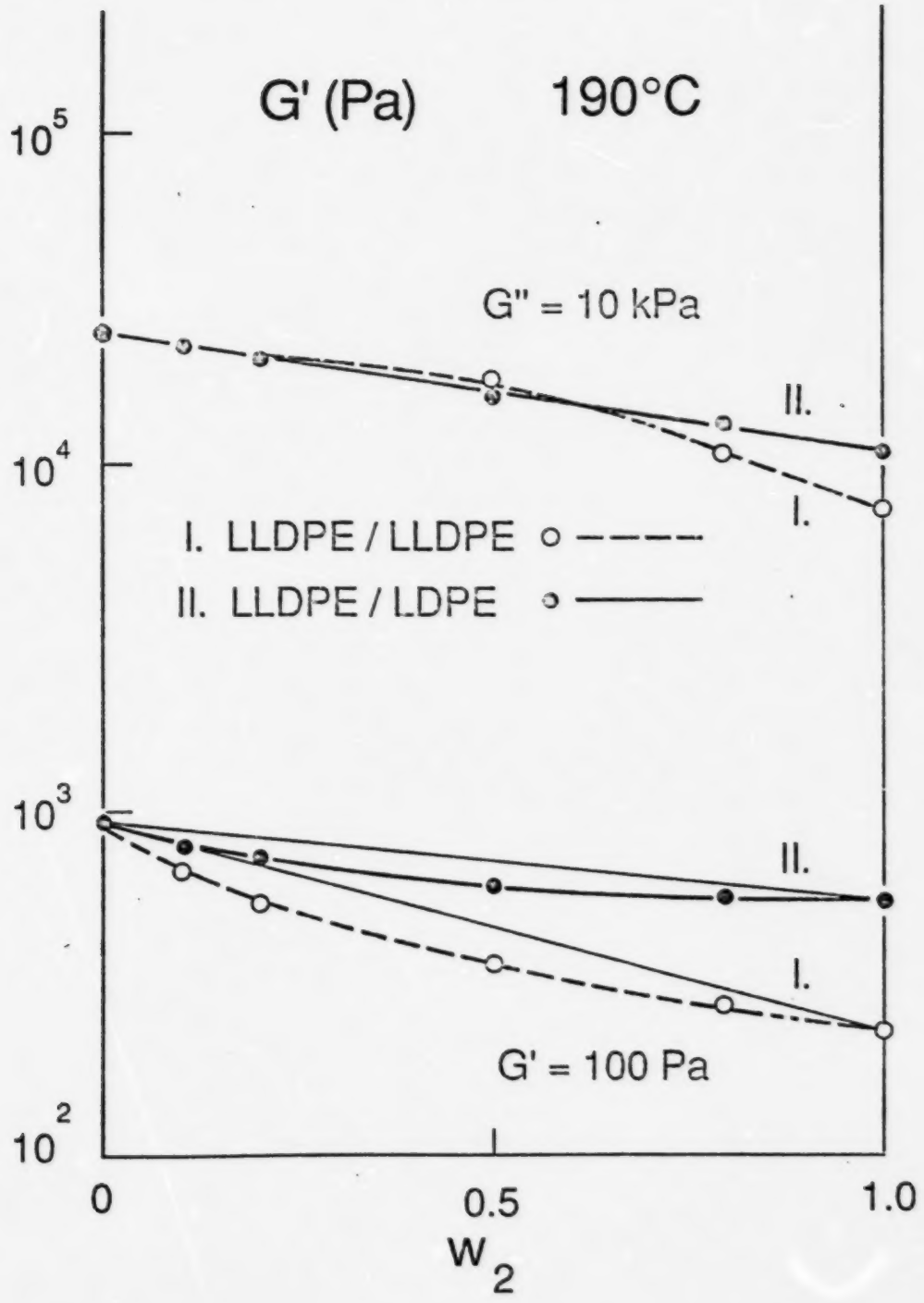

(b)
ΔG
12 m
0
-12
log η
POM /CAB
4.5
4.0
3.5
0
0.5
1.0
W POM

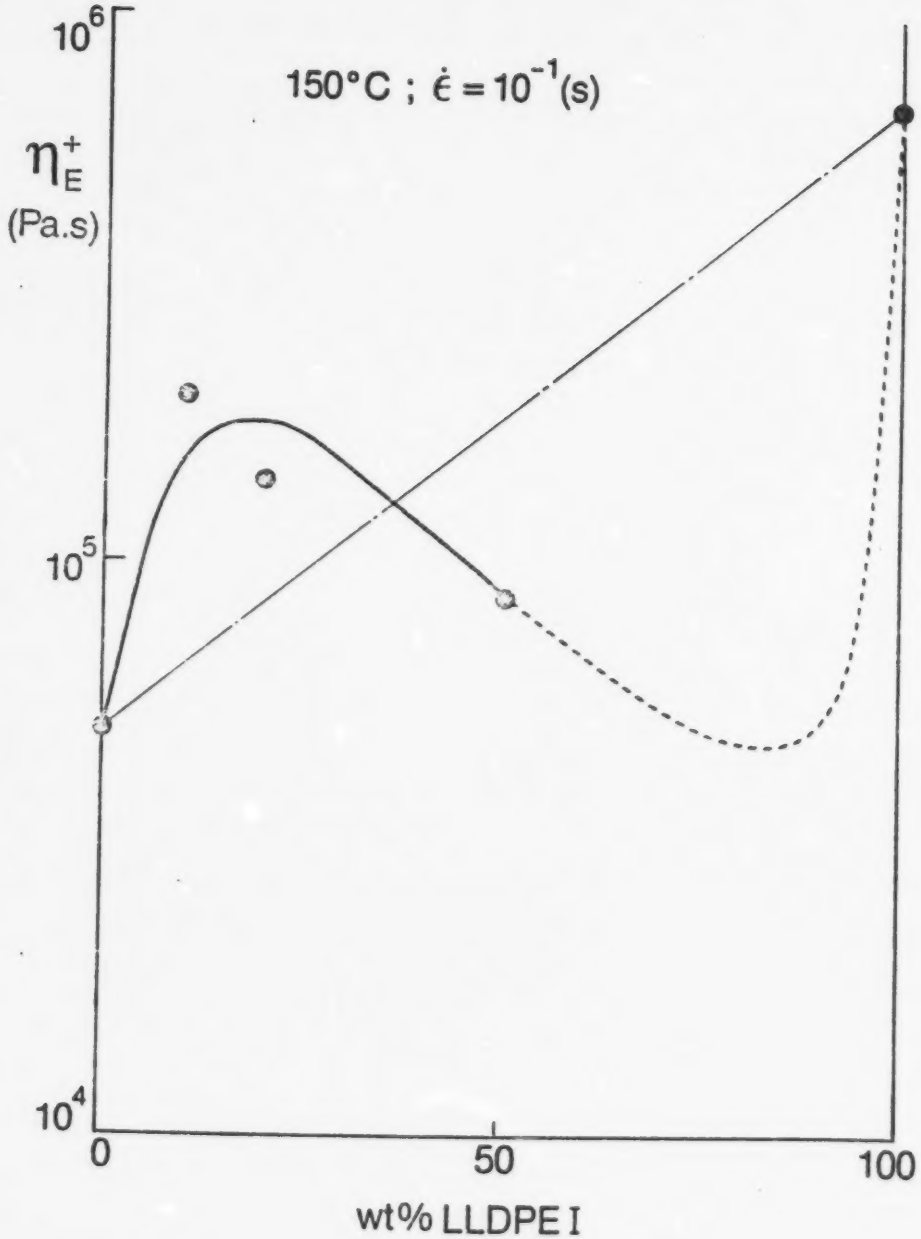
Fig. 18

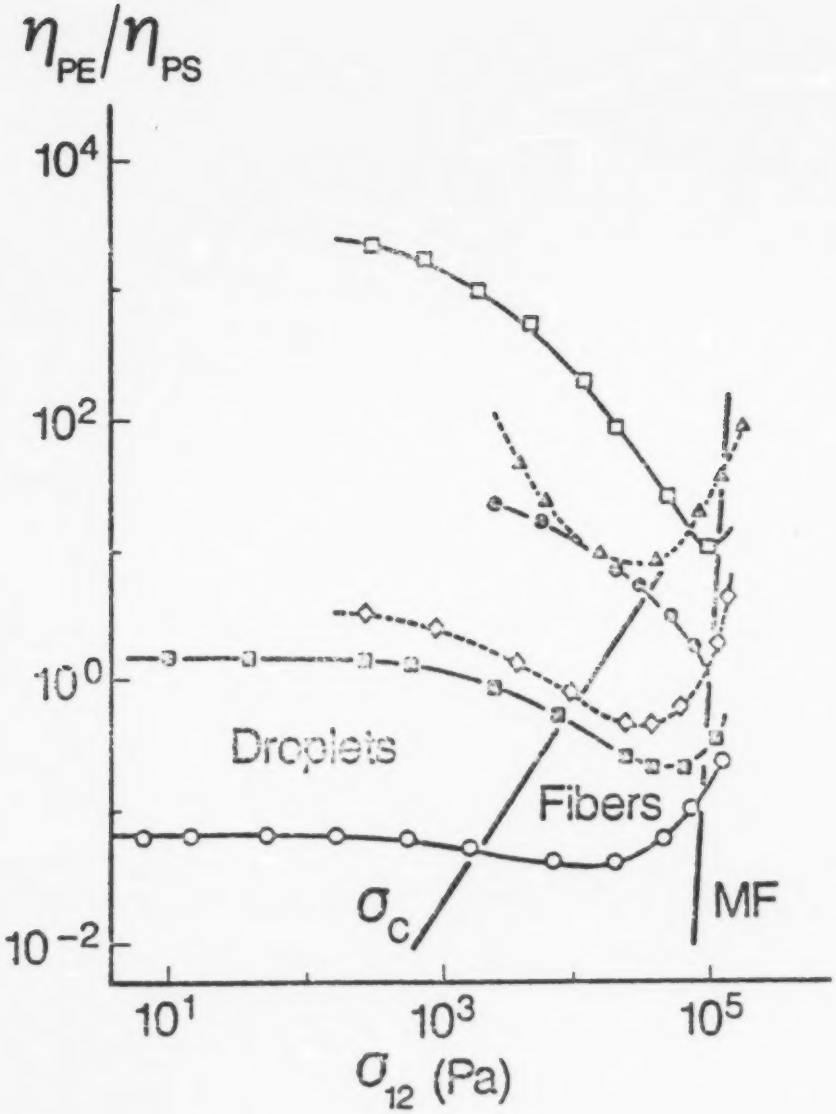

log $\tilde{H}_{G,\,max}$
−0.7
−0.9
−1.1
−1.3
Series - II.
Series - I.
0.1
0.2
0.3
$\frac{M_n}{M_w}$


η''/η0
0.5
0
0
0.5
1.0
η'/η0
1. PC
2. PC / 24 TMPC / 4 PS
3. PC / 35 wt % PS
1
2
3

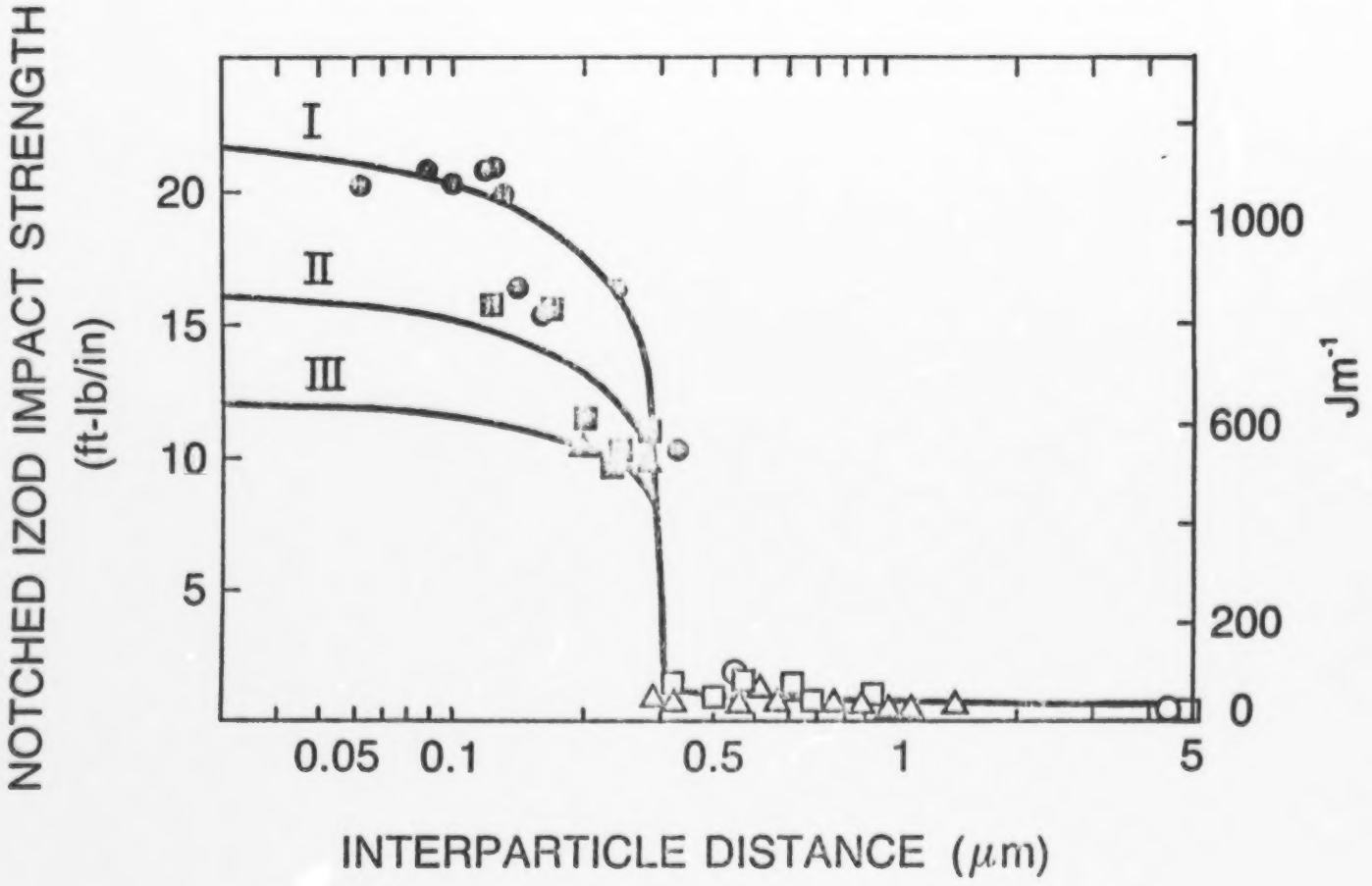

G'(Pa) 190 °C
$10^6$
$10^5$
$10^4$
$10^2$
$10^1$
$10^0$
$\omega = 10^2$
I.
II.
I. LLDPE / LLDPE
II. LLDPE / LDPE
I.
$\omega = 10^{-2}$
II.
0
0.5
1.0
$W_2$

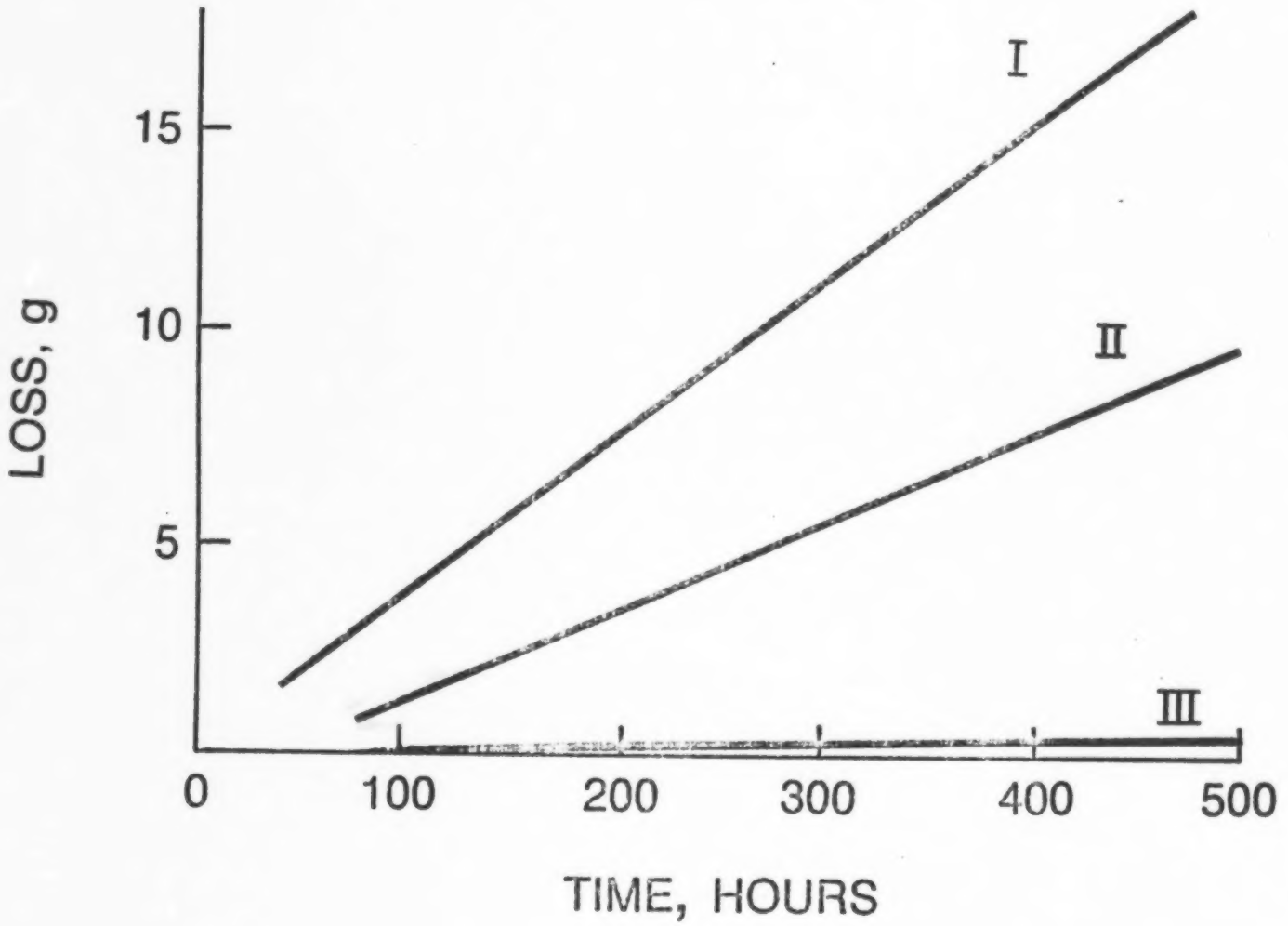

G' (Pa)
190°C
$10^5$
$10^4$
$10^3$
$10^2$
G" = 10 kPa
II.
I.
I. LLDPE / LLDPE
II. LLDPE / LDPE
II.
I.
G' = 100 Pa
0
0.5
1.0
$w_2$


$10^6$
150°C ; $\dot{\epsilon} = 10^{-1}$(s)
$\eta_E^+$
(Pa.s)
$10^5$
$10^4$
0
50
100
wt% LLDPE I

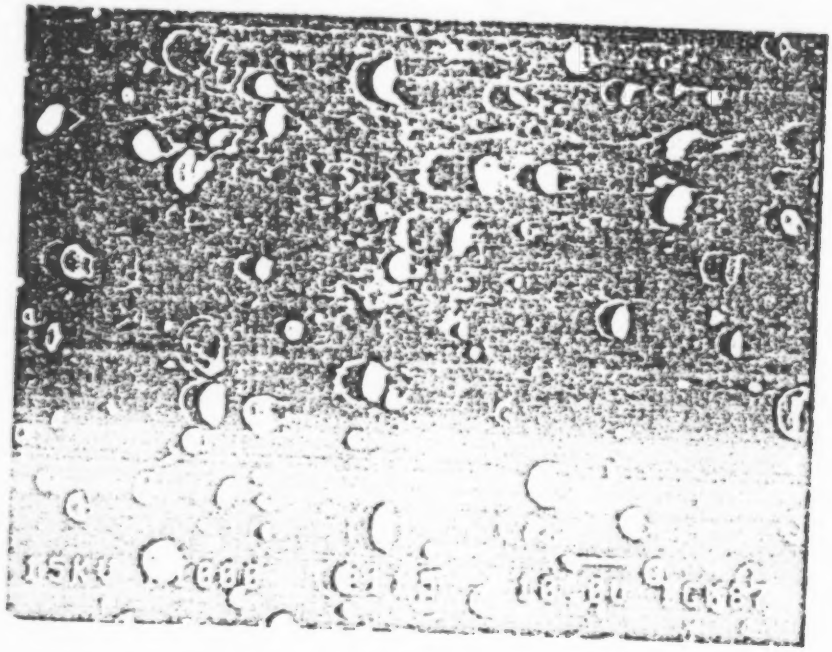

$\eta_{PE}/\eta_{PS}$
$10^4$
$10^2$
$10^0$
$10^{-2}$
Droplets
Fibers
$\sigma_c$
MF
$10^1$
$10^3$
$10^5$
$\sigma_{12}$ (Pa)

NOTCHED IZOD COMPACT STRENGTH
(ft-lb/in)
20
15
10
5
0.2
0,5
1
2
5
RUBBER PARTICLE DIAMETER (μm)
1000
600
200
0
NOTCHED IZOD IMPACT STRENGTH (Jm⁻¹)
I
II
III

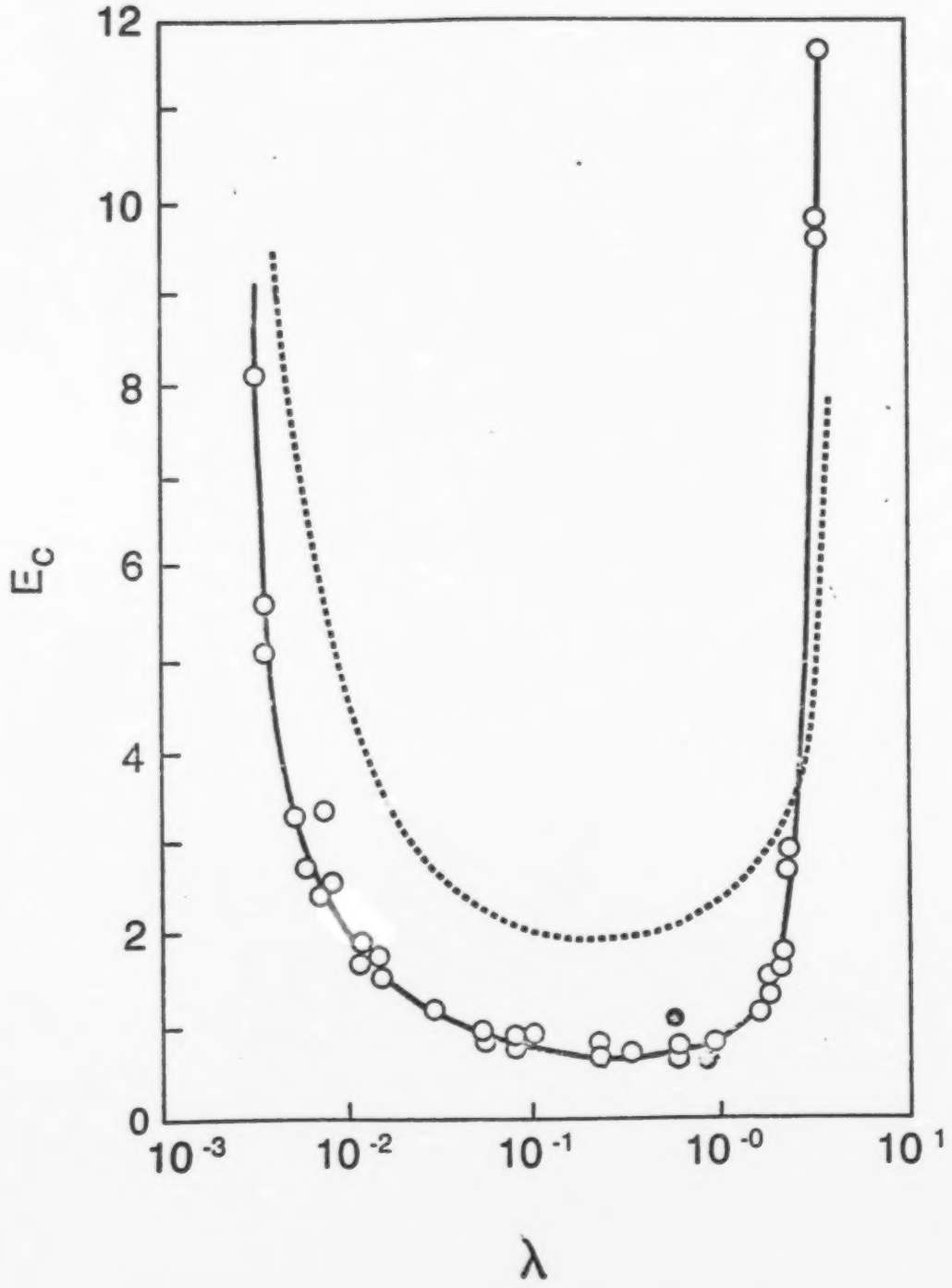

NOTCHED IZOD IMPACT STRENGTH
(ft-lb/in)
20
15
10
5
I
II
III
1000
600
200
0
$Jm^{-1}$
0.05
0.1
0.5
1
5
INTERPARTICLE DISTANCE ($\mu$m)

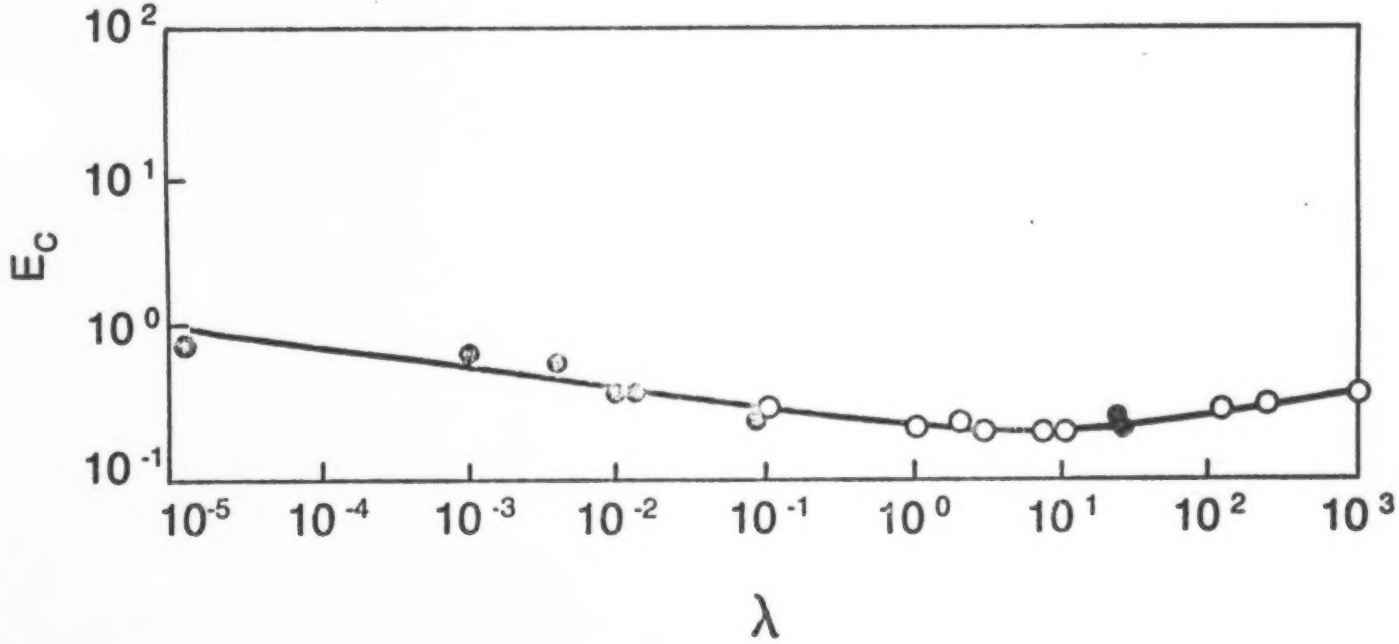

LOSS, g
15
10
5
0
100
200
300
400
500
I
II
III
TIME, HOURS

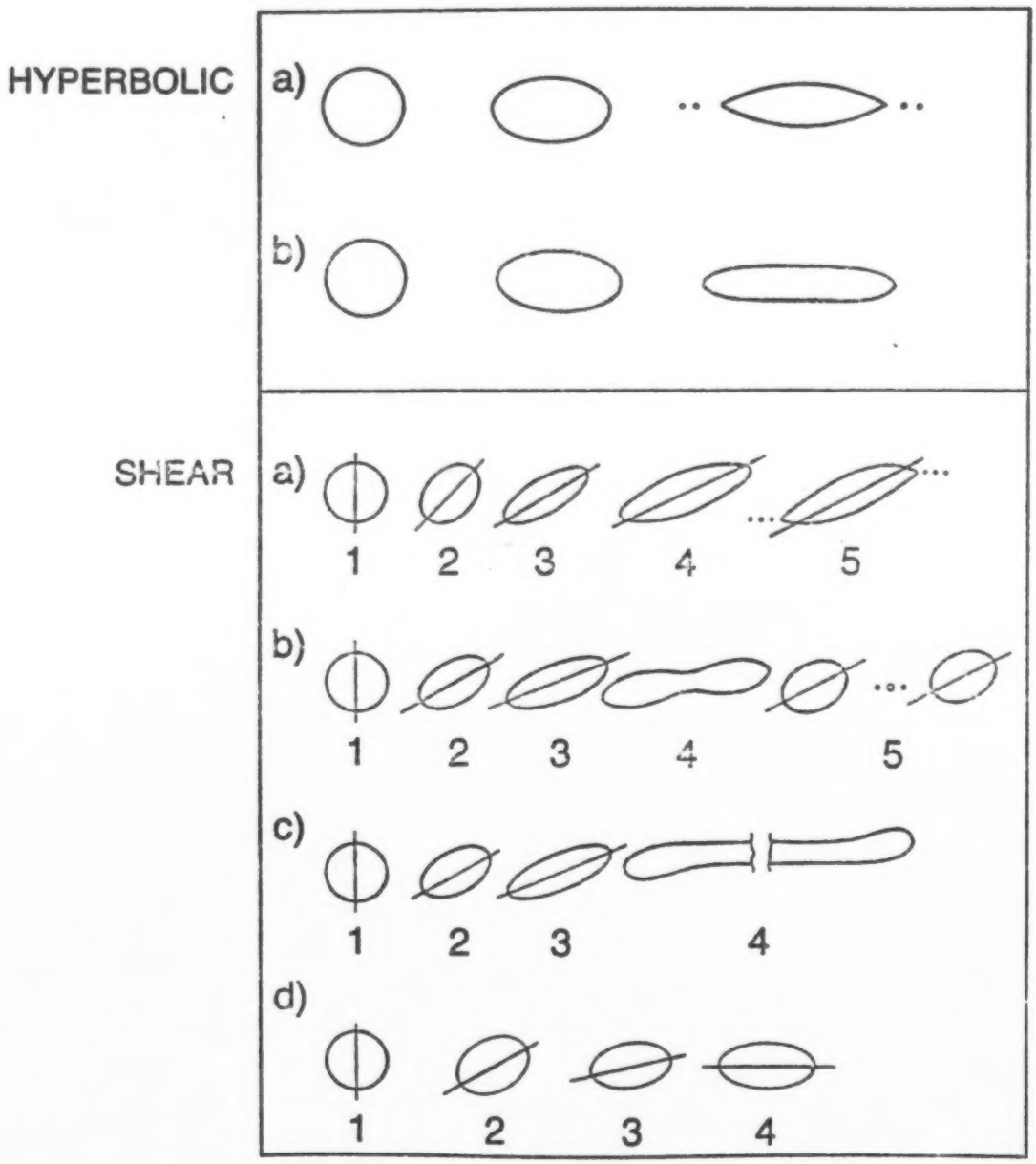
a)

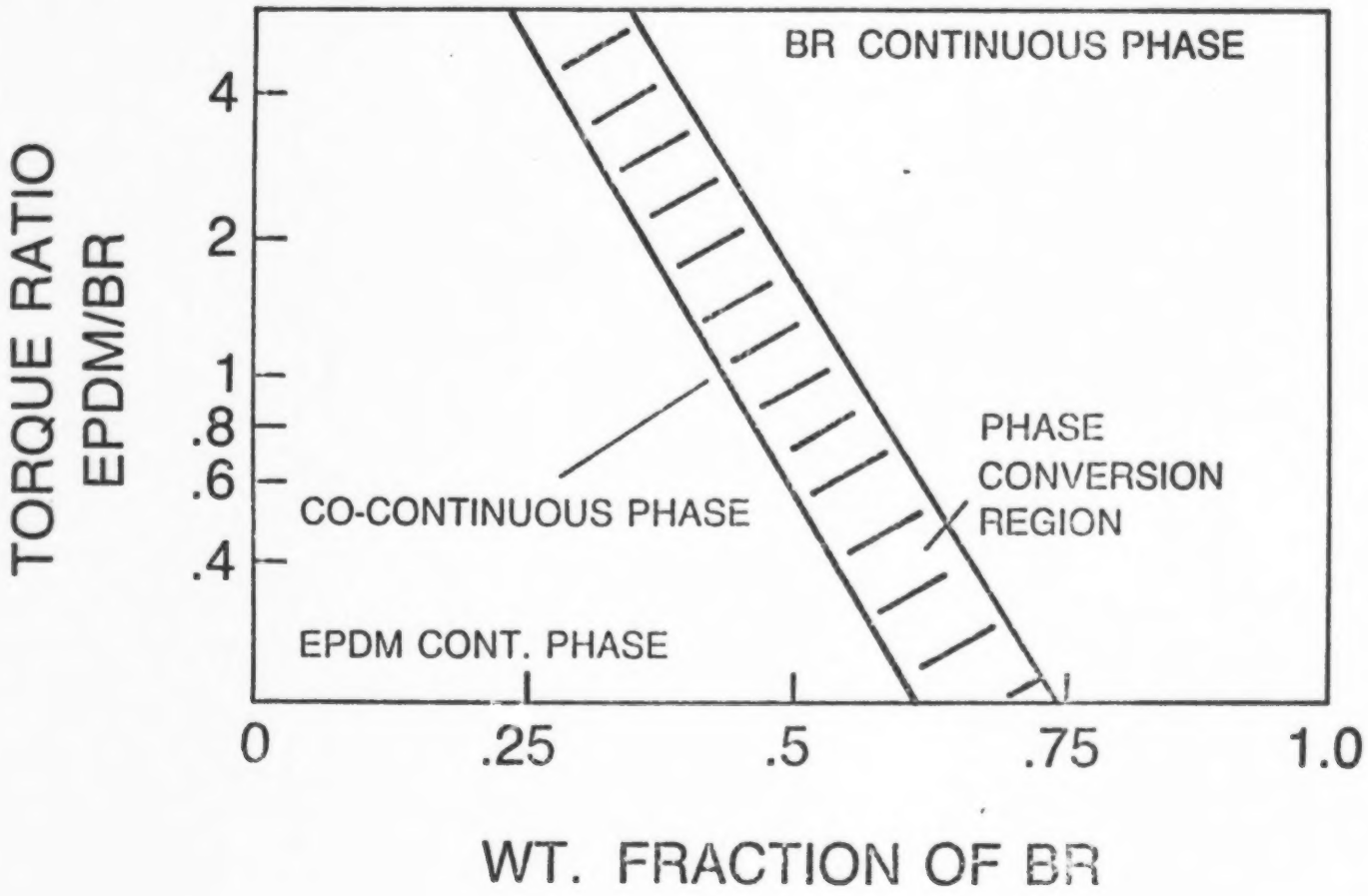


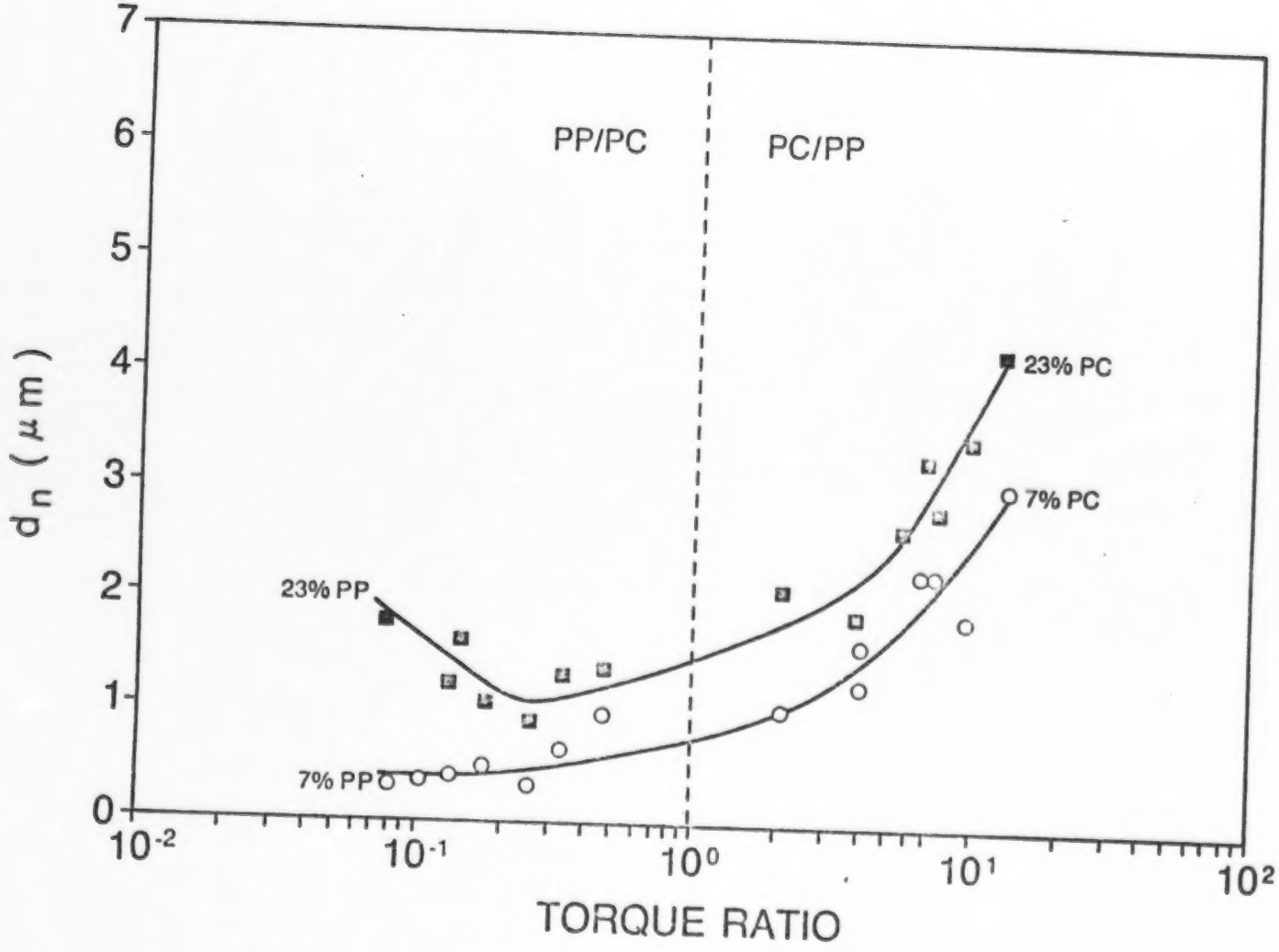
b)

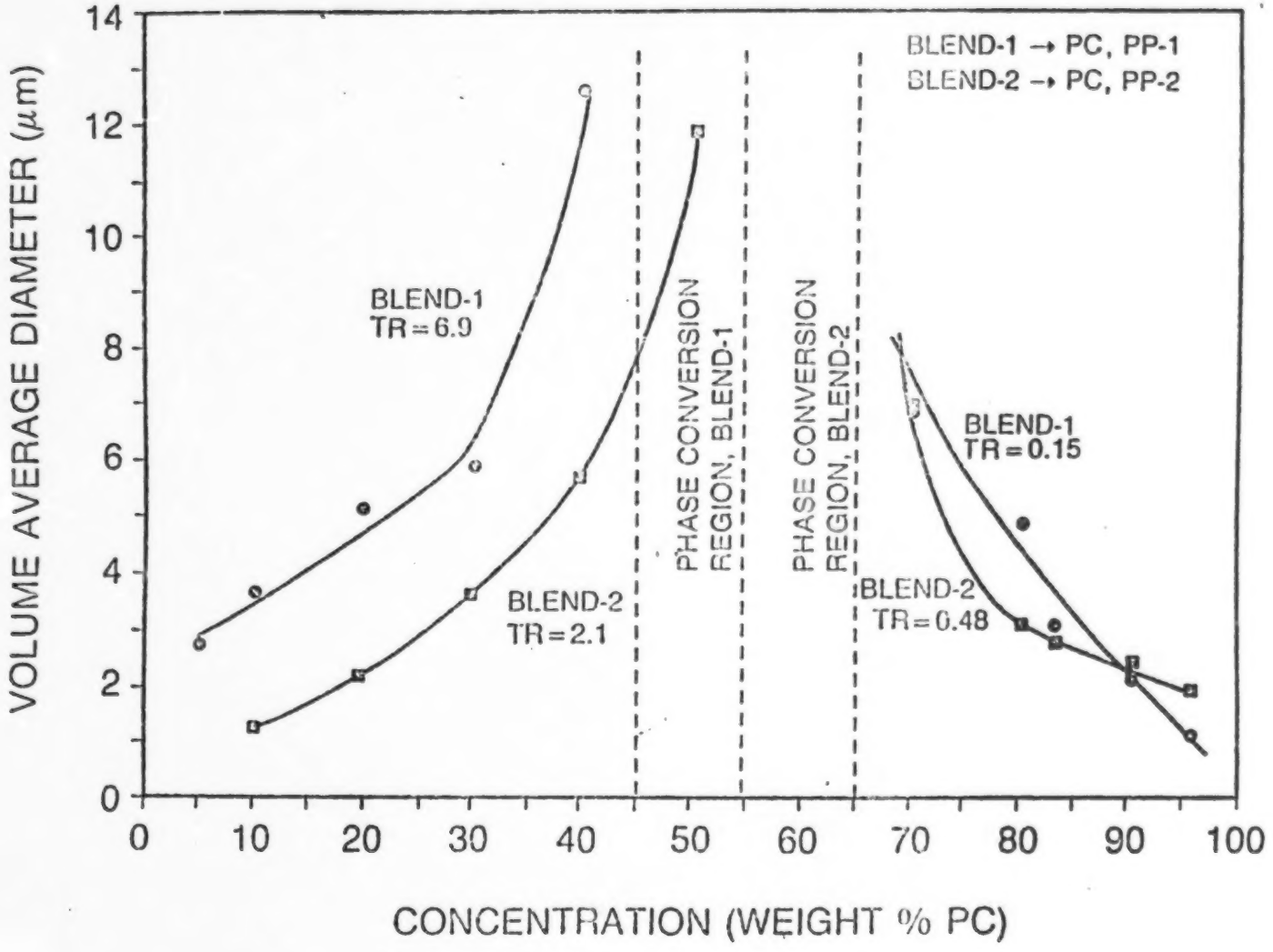

12
10
8
6
4
2
0
$E_c$
$10^{-3}$
$10^{-2}$
$10^{-1}$
$10^{-0}$
$10^{1}$
λ


$10^2$
$10^1$
$10^0$
$10^{-1}$
$E_c$
$10^{-5}$ $10^{-4}$ $10^{-3}$ $10^{-2}$ $10^{-1}$ $10^0$ $10^1$ $10^2$ $10^3$
λ


HYPERBOLIC
a)
b)
SHEAR
a)
1 2 3 4 5
b)
1 2 3 4 5
c)
1 2 3 4
d)
1 2 3 4


BR CONTINUOUS PHASE
CO-CONTINUOUS PHASE
PHASE
CONVERSION
REGION
EPDM CONT. PHASE
TORQUE RATIO
EPDM/BR
4
2
1
.8
.6
.4
0
.25
.5
.75
1.0
WT. FRACTION OF BR


7
6
5
4
3
2
1
0
$d_n$ ( $\mu$m )
PP/PC
PC/PP
23% PC
7% PC
23% PP
7% PP
$10^{-2}$
$10^{-1}$
$10^{0}$
$10^{1}$
$10^{2}$
TORQUE RATIO


BLEND-1 → PC, PP-1
BLEND-2 → PC, PP-2
BLEND-1
TR = 6.9
BLEND-2
TR = 2.1
PHASE CONVERSION REGION, BLEND-1
PHASE CONVERSION REGION, BLEND-2
BLEND-1
TR = 0.15
BLEND-2
TR = 0.48
VOLUME AVERAGE DIAMETER (μm)
CONCENTRATION (WEIGHT % PC)
0
2
4
6
8
10
12
14
0
10
20
30
40
50
60
70
80
90
100